R.L. DUTTA

Inorganic Chemistry

Part-I Principles

THE NEW BOOK STALL

Inorganic Chemistry

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R L Dutta

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The chemists are a strange class
of mortals impelled by an almost insane
impulse to seek their pleasure
among smoke and vapour,
soot and flame, poisons and poverty ;
yet among all these evils I seem
to live so sweetly that I may die
if I would change
places with the Persian King.

Johann Joachim Becher
(1669)

Preface to the Third Edition

In order to make this third edition of the book more useful to the students and their teachers most of the chapters have been carefully revised and updated. Many problems have been worked out with a view to enhancing the confidence of the young students.

I am extremely grateful to Shri Debdas Nath and Shri Mohendra Nath Paul for their advice and cooperation.

It has been a pleasure for me to note the support that the students and teachers all over the country have accorded to the book. I look forward to constructive comments and suggestions from all quarters on this edition as well.

R L DUTTA

Burdwan, West Bengal
July, 1986

Preface to the Second Edition

The book has been thoroughly revised and substantially enlarged maintaining the same chapter lay-out of the first edition. In order to make things easier for the students the book has been split up into two Parts: Part I: Principles and Part II: The Chemical Elements and their Compounds. Several new Appendices have been added at the end of Part II to aid in the understanding of the textual matter. It is hoped that this augmented edition will render better service to the Honours undergraduates of the Indian Universities.

The services of Dr G. P. Sengupta and Dr S. P. Banerjee in the preparation of the manuscript and press materials are gratefully acknowledged. I appreciate the assistance given me by my research associates, Shri S. K. Satapathi and Shri R. Sharma in proof reading. I desire to put on record my indebtedness to Shri Debdas Nath and Shri Mohendra Nath Paul for their playing key-roles in the publication of this revised edition.

I heartily thank all those who had so kindly sent in their comments and suggestions on the first edition. Further comments are welcome.

R L DUTTA

Burdwan, West Bengal
June, 1980

Preface to the First Edition

The book is designed to serve mainly B Sc (Honours) undergraduates of Indian Universities. Some chapters will be useful to M.Sc students as well. An endeavour has been made to show that properties of chemical elements are closely related to their electronic configuration. Orbital hybridisation, molecular orbital and crystal field models have been introduced for a clear understanding of modern inorganic chemistry. Study questions and bibliography are added after each chapter.

I am thankful to Dr S. C. Rakshit, Dr A. K. Chaudhury, Dr A. S. Basu, Dr G. S. De, Shri G. P. Sengupta and Shri S. Sarkar for their comments. I am particularly grateful to Dr S. Ghosh for going through the manuscript and making useful suggestions on the draft. I am also thankful to the management and the staff of M/S Sadhana Press Pvt. Ltd. for cooperation. I wish to record my deep sense of gratitude to Prof. S. R. Palit for encouragement but for which the book would not have seen the light of the day.

Despite my best efforts, some errors might have crept in. Suggestions and criticisms from learned professors and inquisitive students towards improvement will be thankfully received and gratefully acknowledged in the next edition.

R L DUTTA

Burdwan, West Bengal
June, 1973

Abbreviations

A, Angstrom unit, 10^{-8} cm

acacH, acetylacetone

B, Racah interelectronic repulsion parameter

B′, Racah interelectronic repulsion parameter in complexes

BigH, biguanide

B.P., boiling point

BPHAH, N-benzoyl N-phenylhydroxylamine

BPOH, 2-benzoylpyridine oxime

B.M., Bohr Magneton

CFSE, Crystal field stabilisation energy

d, dextrorotatory

DAPDH$_2$ Diacetyl pyridine dioxime

diars, o-phenylene bisdimethylarsine $C_6H_4(As(CH_3)_2)_2$

dien, diethylenetriamine

diglyme, diethyleneglycoldimethylether

dipy, αα′-dipyridyl

DMGH, dimethylglyoxime

DMSO, dimethylsulphoxide

E.A., electron affinity

EDTAH$_4$, ethylenediaminetetraacetic acid

en, ethylenediamine

e.v., electron volt

h, Planck's constant

IDAH$_2$, iminodiacetic acid

I.P., ionisation potential

kK Kilokayser ($1\ kK = 1000$ cm^{-1})

l, levorotatory

LCAO, linear combination of atomic orbitals

$LutH_2$, lutidinic acid (pyridine 2, 6 dicarboxylic acid)

MIBK, methylisobutyl ketone

M.O., Molecular orbital

M.P., Melting point

$m\mu$, millimicron (10A)

NicH, nicotinic acid

nm, nanometre (= millimicron)

$OPPH_3$, triphenyl phosphine oxide

OxH_2, oxalic acid

OxinH, 8-hydroxyquinoline

o-phen, o-phenanthroline

PicH, picolinic acid

PPh_3, triphenylphosphine

py, pyridine

QAS, tris (o-phenylarsinophenyl) arsine

QH, quinaldinic acid

salglyH, salicylideneglycine

SBH_2, dibasic tridentate schiff base

$tartH_2$, tartaric acid

TBP, tributylphosphate

THF, tetrahydrofuran

VB, valence bond

χ magnetic susceptibility

μ, magnetic moment in B.M.

ϵ, molar extinction coefficient

λ_{max}, wave length of maximum absorption

Contents

PART 1
PRINCIPLES

The Structure of Atoms

Rutherford had remarked that it is not in the nature of things for any one man to make a sudden, violent discovery. Science goes step by step and every man depends on the works of his predecessor. The chemists and the physicists of the Rutherford era had to draw from the work of their predecessors. The journey from the Daltonian model of the atom to the modern structure of atoms was a long and arduous one. The Daltonian atom was conceived to be an indivisible particle capable of independent existence. An atom was considered the smallest building block of matter and nothing smaller existed. A scrutiny of the developments after Dalton raised doubts about the validity of the indivisibility of the atom. At the turn of this century many valuable informations were being compiled, which clearly indicated that Dalton's atom no longer enjoyed the exalted position granted to it; instead these results showed that an atom was composed of further subatomic particles such as electron, proton and neutron. Today an atom is considered to be made up of a tiny nucleus carrying neutrons and protons. This tiny nucleus has around itself a certain number of negatively charged particles of negligible mass, called electrons, arranged in a definite order. These extranuclear electrons were earlier thought to be rotating around the nucleus in some definite, permitted orbits, and while doing so there was no emission or absorption of energy. Today the electrons are considered to give rise to standing waves, and we can at most talk of the probability of discovering a particular electron in certain region of space around the nucleus, called orbitals.

Electrons hold the key to the chemical world. Our present day understanding of the chemical elements and their properties rests primarily on the electronic structures of the elements. A chemical reaction is the outcome of some change in the electronic arrangement of the reactant atoms. We can hardly afford to ignore the enormous importance of the electronic structures of atoms. So we begin our study of the inorganic chemicals with a discussion of the structure of atoms.

1.1. THE COMPONENTS OF ATOMS: ELECTRONS AND NUCLEI

1.1.1. The Electrons. That atoms can be split further into subatomic funda-
mental particles was convincingly demonstrated by experiments involving the
conduction of electricity through gases at low pressures. Gas discharge tubes
are provided with a negative electrode (*cathode*) and a positive electrode (*anode*),
with provisions of evacuation. Under normal conditions gases are poor conductors
of electricity. At reduced pressures, however, conduction occurs. When discharge
tubes are partially evacuated and the cathode and the anode are connected to a
source of high voltage (spark coil), an electric current flows through the tube.
This flow of electricity is associated with a glow or rays of light which have their
origin at the cathode surface. These rays travel from the cathode to the anode.
Since they originate from the cathode they are called cathode rays.

The properties of these cathode rays were extensively investigated by Thomson
for over twenty years. Thomson showed that these rays could be bent from their
path both by electric and magnetic fields, and hence the rays must carry electrically
charged particles. He could prove from the direction of bending that the *cathode
rays were made up of negatively charged particle*. He called them *electrons*.

Thomson measured the charge to mass ratio, e/m, of the electrons. Millikan
determined the absolute charge of the electron. He found that tiny oil drops in
ionised air would tend to pick up an electric charge and could then be debarred
from falling under gravity by the application of an electric field of appropriate
intensity and direction. The charges acquired by the drops were found to be multi-
ples of some smallest charge. This smallest charge was considered to be associated
with a single electron. In usual units this charge is $e = 1.6 \times 10^{-19}$ *coulombs*/
electron ($= 4.8 \times 10^{-10}$ *esu*/electron). Thomson's experiments gave e/m of the
cathode rays as 1.76×10^8 coulombs/gm so that the mass of an electron becomes
9.108×10^{-28} gm/electron. The electric charge carried by the electron is expressed
in the arbitrary relative value of -1; a unit negative charge -1, therefore, carries
with it the absolute value of $e = 1.6 \times 10^{-19}$ *coulomb*/electron $= 4.8 \times 10^{-10}$ *esu*/
electron $= 1.6 \times 10^{-20}$ *emu*/electron. (Velocity of light $\simeq 3.0 \times 10^{10}$ cm/sec).

The mass of the electron as given above is the *rest mass* which is valid as long
as the velocity of the electron is not too great. The usual speed of an electron is
about one-tenth of the velocity of light. Although this speed of the electron is
still very high, the electron is considered to be at rest compared to light. It is
interesting to note that experiments on the e/m of electrons of varying speed (as
with beta-rays of different origins) have shown that e/m value decreases slightly
with increased velocity of the electron. The charge e of the electron being pro-
bably quite independent of the velocity, the obvious conclusion is that *with increas-
ing speed the mass of the electron increases*. The following mathematical relation
describes the change of mass with changing velocity of a particle:

$$m = m_0 (1 - v^2/c^2)^{-\frac{1}{2}}$$

where m_0, v, and c stand for the rest mass of the electron, velocity of the electron
and the velocity of light respectively.

Thomson had also developed an equation connecting radius (r), mass (m) and charge (e) of a spherical, charged particle:

$$r = \frac{2e^2}{3m}$$

This Thomson equation needs some elaboration. The e is expressed in *emu* units and the mass is considered to be electromagnetic in orgin. A particle is considered to possess mass whenever energy is to be supplied to set it in motion. A moving charged particle such as the electron creates a magnetic field. The magnetic field is created at the expense of energy and this energy has been supplied to the electron while setting it into motion. Since the electron has an electric charge and can generate a magnetic field (while in motion) it has an electromagnetic mass. Putting the appropriate values of e and m of an electron, the radius of an electron worked out to be $\sim 2.0 \times 10^{-13}$ cm.

The existence of electrons has since been confirmed in many other experiments. Heavy atom nuclei, such as those of uranium, radium, polonium, etc. undergo spontaneous disintegration into nuclei of other atoms. Such disintegration processes are accompanied by radiation, and form the subject matter of a separate chapter on radioactivity. These radiations are due to spontaneous release, from inside the nuclei, of *alpha particle* (doubly charged helium ion He^{2+}), *beta particle* (an electron) or *gamma ray* (short wave length rays). Electrons are also emitted by active metal surfaces at high temperature (*thermionic emission*) or upon irradiation of a metal surface by light of short wave length (photoelectric emission). Addition or removal of electrons to or from atoms is also the basis of electrolysis. Electrons are known to play a key role in chemical reactions.

Thomson's determination of e/m of the electron. The electron beam originating from the cathode C (Fig. 1.1). passed through a hole in the anode A. A narrow beam of the electrons was selected with the help of the slit S. The plates PP could be connected to a source of high potential and thus an electric field applied to the electron beam. An electromagnet M outside the tube provided the necessary magnetic field.

FIG. 1.1. Thomson's apparatus for determination of e/m of electrons.

Consider a stream of negatively charged particles, each with the same charge e and mass m moving in a straight line with a velocity v. If a magnetic field (H) is applied at right angles to the direction of the beam, the magnetic force experienced by each particle is Hev. The electrons will describe a circular path of radius r

under the influence of this force. The centrifugal force mv^2/r will be equal and opposite to the magnetic force. Thus,

$$Hev = mv^2/r \text{ and } e/m = v/Hr$$

If an electric field, X, is applied to an electron the force on the electron will be Xe. Now the experimental conditions are so adjusted that the magnetic and electric field work in opposition and that there is no deflection from the original direction of the beam. Then,

$$Hev = Xe; v = X/H \text{ and } e/m = X/H^2r$$

The position F of the undeflected electron beam in the absence of electric or magnetic fields was first noted on the far end of the apparatus. The magnetic field was then applied and from the deflection to G the radius of curvature of the path was calculated. The electric field was then applied and adjusted so as to bring the electron beam back to its original position. The strengths of the magnetic and electric fields for no deflection allowed the calculation of e/m.

FIG. 1.2. Evaluation of r

Evaluation of r from the dimension of the apparatus: The radius of curvature, r, can be evaluated following Fig. 1.2.

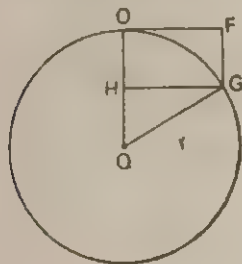$$\begin{aligned} OF^2 = HG^2 = QG^2 - HQ^2 &= r^2 - HQ^2 \\ &= r^2 - (OQ - OH)^2 \\ &= r^2 - (r - FG)^2 \\ &= r^2 - r^2 + 2r\,FG - FG^2 \\ &= FG\,(2r - FG) \end{aligned}$$

Thus with a knowledge of OF and FG the radius of curvature, r, can be obtained.

The same e/m was obtained irrespective of the nature of the gas present inside the cathode ray tube or of the material of the cathode. This striking constancy of e/m for negatively charged particles under a variety of conditions suggested that the cathode rays were all made up of the same particle, electron, and they were the carriers of electricity.

Millikan's determination of the electronic charge. Millikan essentially devised a technique of studying the rate of fall of tiny oil droplets in thermostated chamber under the influence of gravity and under the influence of an applied electric field. Because of the gravitational force, the droplet fell through the atmosphere of the chamber with a uniform velocity which was determined by the size of the droplet and by the temperature and pressure in the chamber. The electric field was applied by connecting two metal plates A, B (Fig. 1.3) fixed to the lower half of the chamber and a few centimetres apart, to sources of high voltage. The upper metal plate A, had quite a number of very small holes through which oil droplets could enter the space between the charged plates. By means of an atomiser a fine spray of a non-volatile oil was introduced into the chamber. By changing the electric potential difference it was possible to alter the velocity of fall

of the oil drop, to make the drop stand still or even to make it travel upwards. Millikan ionised the air in the chamber by application of X-rays so that the oil drops could attach to gaseous ions, thus acquiring a charge. The movement of the oil drop was followed by a telescope to which were attached two sets of crosswires.

If v_1 is the rate of fall of the drop under the influence of gravity and v_2 the rate of upward travel under an electric field of strength X acting in opposition to gravity, then

$$\frac{v_1}{v_2} = \frac{m_d g}{Xe_n - m_d g}; \quad e_n = \frac{m_d g (v_1 + v_2)}{Xv_1}$$

where m_d is the mass of the drop, e_n the charge it carries and g, the acceleration due to gravity. Since the weight remains constant, v_1 (velocity in the absence of electric field) should remain constant. But v_2 may change if the charge e_n carried by the drop changes in successive journeys. The results showed that e_n changed often. The two velocities v_1 and v_2 were found out from a knowledge of the time taken by the oil drop to travel the known distance corresponding to the gap between the two sets of crosswires of the telescope. The charge of the oil drop could be calculated from the above relation provided the mass of the drop was known. The mass was calculated from v_1 using the following relation:

$$v_1 = \frac{2gr^2}{9\eta} \left(\rho_d - \rho_a \right) \left(1 + A\frac{\lambda}{r} \right)$$

where r is the radius of the drop, ρ_d and ρ_a are the densities of the drop and of air, η is the viscosity of air, λ is the mean free path of the air molecules and A is an empirical constant. Once r is known the volume ($4/3\pi r^3$) of the drop is also known. Now the density ρ being also predetermined, mass m_d, is given by the product of the volume and density.

If the variation of upward velocity under the influence of the electric field is due to differences in the charge carried by the oil drop and if this charge is always an integral multiple of a single unit, presumably the charge of the electron, the values of e_n must always be a multiple of the smallest charge observed. This smallest charge was found to be 1.6×10^{-19} *coulombs*/electron ($= 4.8 \times 10^{-10}$ *esu*/electron).

Coulometric determination of the electronic charge: During electrolysis of aqueous solution of a *suitably chosen metal salt* a deposit of the metal takes place on the cathode. A monopositive cation M$^+$ acquires an electron from the cathode, changes to neutral M and is then deposited on the cathode. It therefore follows that electrodeposition of one mole of a monopositive cation will need one mole
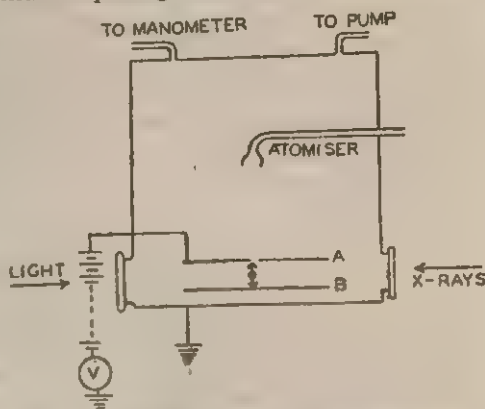
FIG. 1.3. Millikan's apparatus for determination of the electronic charge.

of electrons. Thus if we know precisely the quantity of electricity (charge) that passes through the solution during a fixed time and also know from the initial and final weights of the cathode the amount of the metal deposited on the cathode during the same time interval we can calculate the charge associated with a single electron.

Electrodeposition of silver from an aqueous solution of a silver salt is a suitable experiment for the determination of the electronic charge. A constant current I (amperes) is passed through a solution of silver nitrate during a time t (seconds). Then: Number of coulombs of charge $= I \times t$ (1 coulomb $=$ 1 ampere sec). Number of coulombs required to deposit of 1 gm. of silver.

$$= \frac{\text{number of coulombs passed during time } t}{\text{grams of silver deposited during time } t}$$
$$= 894.5 \; coulombs/gm. \text{ of silver (experimental result)}$$

If we multiply this figure by the gram atomic weight of silver i.e., by the mass of 1 mole of silver we have the number of coulombs necessary for the deposition of one mole of silver:

$(894.5 \; coulombs/gm) \times (107.9 \; gm/mole) = 96,500 \; coulombs$ per mole. Electrolysis experiments reveal that the coulombs required for the deposition of one mole of other ions are either 96,500 or integral multiples of 96,500.

Metal electrodeposited	Coulombs/mole
Ag	96,500
Na	96,500
Cu	193,000
Mg	193,000

The charge of 96,500 coulombs can thus be considered as the charge carried by a mole of electrons. 96,500 coulombs go by the name 'faraday' after Michael Faraday who did the pioneering studies on electrolysis. Now since a mole means the Avogadro number we have:

Charge associated with an electron

$$= \frac{96,500 \; coulombs}{\text{mole of electrons}} = \frac{96,500 \; coulombs}{6.02 \times 10^{23} \text{ electrons}}$$
$$= 1.60 \times 10^{-19} \; coulomb/electron = 4.8 \times 10^{-10} \; esu/electron$$
$$= 1.60 \times 10^{-20} \; emu/electron.$$

1.1.2. The Positron and Wilson Cloud Chamber. Since the discovery of the electron scientists were immensely interested in identifying its positive counterpart —the *positron*. In ordinary matter they could find only a particle with a unit positive charge but a mass of about 1840 times that of an electron. This particle was named *proton* (see later). However the positron was traced out to be present in cosmic rays originating in outer space. The identification of the positron was done with the help of Wilson cloud chamber.

Wilson cloud chamber is a chamber provided with a piston. The chamber is filled with dust-free air saturated with water vapour. On sudden expansion (by controlling the piston) the temperature drops and the water vapour condenses. If a charged particle moves through the chamber it will ionise the molecules in its

path and water drops will condense on the ions. Against a dark background and with proper illumination the path of the charged particles can be photographed as a *cloud track*. The chamber can be placed in a magnetic field and the path of the charged particles may be studied.

The path of electrons in an applied magnetic field was studied in a Wilson cloud chamber. The positrons in cosmic rays were observed to give a curvature opposite in direction to that given by electrons in an applied magnetic field. It was observed that the electrons and positrons on passing through a lead plate of a few mm. thickness (placed inside the cloud chamber) showed the same degree of curvature but in opposite direction. The curvature and the length of the path traversed after passing through the lead plate was several times more in the case of positrons than in the case of protons.

1.1.3. The Nuclei. Rutherford and his students described some alpha particle scattering experiments that profoundly influenced our conception of atoms. The alpha particles were already established by the group as He^{2+} from their behaviour in electric and magnetic fields. A beam of alpha particles, obtained from spontaneously disintegrating polonium, was directed on to a very thin foil of platinum or gold. With the help of a fluorescent zinc sulphide screen around the platinum or gold foil, any deflection of the alpha particles was observed. The vast majority of the alpha particles passed straight through the foil. But a very limited few were found to be deflected (Fig. 1.4) back from the foil, some even appearing on the side of incidence. Rutherford concluded that since most of the alpha particles passed straight through there must be a very large volume of empty space in the atom of platinum or gold. A very small part of the platinum or gold atom must be responsible for the large scattering of the very few alpha particles, and this small part must be very dense and positively charged. This small, central part was called the atomic nucleus.

Rutherford worked out mathematically the laws that the scattering should obey and found that the number of alpha particles scattered through a given angle was proportional to the thickness of the foil, the square of the nuclear charge and inversely proportional to the fourth power of the velocity of the alpha particle. Thus nuclei of high charge deflected more alpha particles through a given angle than nuclei of lower charge. Such alpha particle scattering experiments were done with thin foils of many different elements, with results conforming to Rutherford's derivation of the scattering laws.

A knowledge of the dimension of the nucleus can be obtained as follows:

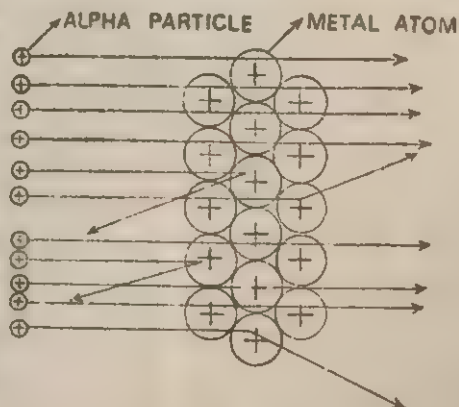The charge on the alpha particle is $2e$ and that on the nucleus is Ze. The

Fig. 1.4. Scattering of alpha particles by atomic nuclei.

repulsive force between the alpha particle and the atomic nucleus is $2Ze^2/r^2$, r being the separation between the atomic nucleus and the alpha particle. The potential energy of the system is $2Ze^2/r$ whereas the kinetic energy of the alpha particle is $\frac{1}{2}mv^2$. It is a reasonable assumption that one alpha particle will reverse its path when its kinetic energy is equal to the potential energy due to repulsion. The distance r at which this occurs is given by $\frac{1}{2}mv^2 = 2Ze^2/r$, where r is the effective radius of the nucleus. The mass m of the alpha particle is four times that of the hydrogen atom which again is 1838 times heavier than an electron ($m = 4 \times 1838 \times 9 \times 10^{-28}$ gm/alpha particle). The velocity of alpha particles is $\sim 2 \times 10^9$ cm/sec. Taking $Z = 10$ and e as 4.8×10^{-10} esu the value of r is found to be $\sim 3 \times 10^{-13}$ cm. It is interesting to note that an electron also has a radius of the same order.

The following conclusions, and an atomic model emerged from Rutherford's experiments;

1. All the positive charge and almost the entire mass of the atom was concentrated in a very small, central core called the atomic nucleus.

2. The large deflection of an alpha particle from its original path was due to Coulombic repulsion between the alpha particle and the positive nucleus of an atom. Simple impact between two such massive particles can lead to a scattering of the order of only about 1°.

3. An alpha particle suffers little deflection while passing by an electron.

4. The radius of an atomic nucleus is $\sim 10^{-13}$ cm, being the same as that of an electron. Since the radius of an atom is $\sim 10^{-8}$ cm it is obvious that an atom must have a very empty structure.

5. An atomic model was proposed by Rutherford: a very small positive nucleus was considered surrounded by electrons. Such a system cannot be stable if the electrons were at rest. Therefore it was proposed that the electrons were moving in circular orbits around the nucleus so that the Coulombic attraction between the nucleus and the electron was equal to the centrifugal force on the electron.

1.1.4. X-ray Spectra and Atomic Number. Although Rutherford's alpha ray scattering experiments allowed a determination of the positive charge of the nucleus the identity of the nuclear charge and atomic number of an element was established by X-ray spectral data obtained by Moseley.
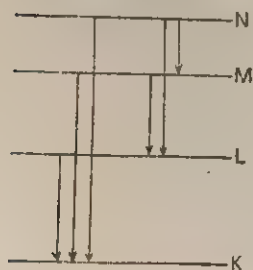

FIG. 1.5. Formation of characteristic X-rays.

When a beam of high energy electrons falls on a metal target, the atoms of the metal are excited, and emit radiant energy. The incident electron beam raises some electrons of the atom of the metal target to different excited levels. Some electrons may even be completely expelled from the atom. The vacancies thus created are now filled up by electrons of higher levels moving in to occupy the lower energy levels. This movement results in emission of energy. The rays constituting the radiant energy are composed of electromagnetic waves and are comparable to light waves. They have

been called X-rays. X-rays are not charged and are not deflected in electric or magnetic fields. Since X-rays are emitted as a result of an interaction of an electron beam and a metal target it occurred to Moseley that a study of the X-rays originating from different metal targets may furnish fundamental informations about the structure of the elements. Each element was expected to produce a characteristic X-ray spectrum. Moseley examined over thirty metal targets from aluminium to gold. Where the elements themselves could not be used as targets (e.g. bromine), the target to be bombarded with electron beam was coated with a suitable compound of the element.

Prior to Moseley's work Bragg had shown that crystals can act as diffraction gratings for X-rays, since the spacing of atoms and molecules in crystals is of the same order as the wave length of the X-rays. Following the technique developed by Bragg for measuring the wave length of X-rays, Moseley analysed the X-radiation by using a crystal of $K_4Fe(CN)_6$ as a diffraction grating. The frequency of the characteristic X-ray radiation could be calculated. It was observed that characteristic X-rays of an element consisted of groups of rays of different frequencies. When a high energy electron beam ejects an electron from the first, most stable, deep seated level of an atom of the target element, an X-ray spectrum is produced as a higher level electron drops down to the first level. This X-ray belongs to the K series. When an electron from the second level is ejected, the X-ray spectrum thus produced belongs to the L-series and so on (Fig. 1.5). The energy decreases from K to L, then to M etc. The K lines are given by elements of low atomic weights, the L lines by copper onwards while the M, N, etc lines by heavier elements only. In attempting to find a relationship between the wave lengths of the emitted X-radiation of an element and its other properties, Moseley plotted the square root of the reciprocal of the shortest observed wave-length $(1/\lambda)^{\frac{1}{2}}$ for each element against its atomic weight. A straight line was obtained but
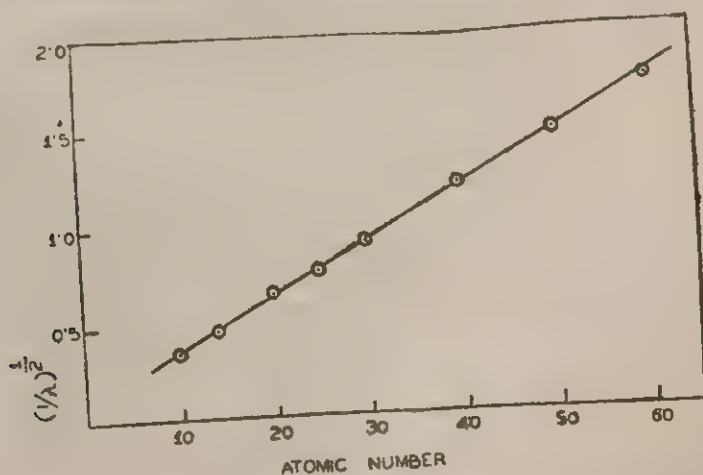

FIG. 1.6. Linear relation between atomic numbers and square root of the X-ray frequency.

the points of a few elements were off the line. A better plot (Fig. 1.6) was obtained when the atomic weights were replaced by the *order number* (*serial number*) of the elements in the Periodic Table. The frequency v of the line belonging to any characteristic X-ray series was found to be related to the atomic number Z of the element as:

$$\sqrt{v} = a\,(Z-\sigma)$$

where 'a' is a proportionality constant and σ is the screening constant. The magnitude of the screening constant indicates the extent to which the full nuclear charge of an element is hidden from the electron in a particular shell. For a particular group of characteristic X-rays σ is a constant so that $(\bar{v})^{\frac{1}{2}} = (1/\lambda)^{\frac{1}{2}}$ should obey a linear relation with the atomic number.

As the atomic numbers of the elements increase, the wave lengths of the characteristic X-rays decrease. Moseley concluded that there is a fundamental quantity in an atom which increases in regular steps with increasing atomic number and that this was the charge of the positive nucleus. The most reasonable interpretation of Moseley's work can be made if the atomic number of an element is taken as equal to the charge on its atomic nucleus. Realisation of this identity of atomic number and nuclear charge brought to light that in order to maintain electroneutrality the atom must carry extranuclear electrons whose number must equal the atomic number. The atomic number of sodium is eleven and, therefore, it must carry eleven positive charges in the nucleus and eleven extranuclear electrons. *A good correlation between X-ray spectra and atomic number, but not atomic weight, further indicated that an element is characterised by its atomic number and not by atomic weight. The properties of an element are dictated by its atomic number and so by the number of its electrons, specifically by their arrangement outside the nucleus.*

In the above correlation it is imperative that each positive charge of the nucleus involves an absolute charge equal but opposite to that carried by one electron.

1.1.5. The Structure of the Atomic Nuclei. Since the extranuclear electrons contribute negligibly to the total mass of the atom and since atom is electrically neutral it follows that the nucleus must carry particles which will account both for the mass and the positive charge of the atom. We have so far deliberately restricted the discussion on discharge phenomena at low gas pressure. The production of cathode rays in discharge tubes inspired physicists to look for oppositely charged ions, namely positive ions. Goldstein added a new feature to the discharge tubes by using holes in the cathode. With this modification, it was observed that on operating such discharge tubes there appeared not only the cathode rays travelling from the cathode to the anode but also a beam of positively charged ions travelling from around the anode to the cathode. Some of the positively charged particles passed through the hole in the cathode and produced a spot on the far end of the discharge tube.

The nature of these positive rays was extensively investigated by Thomson. It proved much more difficult to analyse the beam of the positive rays than to analyse a beam of electrons. On deflection by a magnetic and electric field the positive ray beam produced a large diffuse spot indicating that the e/m ratio of the constituents of the beam was not the same and that the particles moved with different velocities. Thomson further demonstrated that each different gas placed in the apparatus gave a different assortment of e/m.

Using hydrogen inside the gas discharge tube Thomson observed two spots with different angles of deflection. Similarly oxygen produced two spots. Analysis of the positive ray pattern was made by Thomson on the basis that each of the particles had a positive charge of one unit and that the one deflected to the largest extent had the smallest mass. On this basis the four spots obtained from hydrogen and oxygen represented particles of masses 1, 2, 16 and 32 corresponding to species H^+, H^+_2, O^+ and O^+_2. The mass ratio of 1 : 16 for H^+ and O^+ ions, and 2 : 32 for H^+_2 and O^+_2 correspond to the mass ratio of hydrogen to oxygen obtained by chemical analysis.

Since a H^+ is produced from a hydrogen atom by the loss of one electron, which has but a negligible mass, it follows that the mass of a H^+ is the same as that of a hydrogen atom (= 1). The particle represented by H^+ is called a *proton*, and is considered a fundamental constituent that accounts for the positive charge of the nucleus. The proton carries with it the absolute charge of $+ 1.6 \times 10^{-19}$ *coulombs*/proton (= 4.8×10^{-10} *esu*/proton) and is given an arbitrary relative value of $+ 1$. The unit positive charge, therefore, represents 1.6×10^{19} *coulombs*/proton or 4.8×10^{-10} *esu*/proton.

Attempts were now directed toward a correlation of atomic mass number (= integer nearest to the atomic weight) and nuclear charge (= atomic number). If A stands for the mass number and Z for the nuclear charge of an element, then Z units of nuclear charge means Z number of protons inside the nucleus. But Z protons can contribute only Z mass units. The shortfall of the $A - Z$ mass units bothered chemists and physicists for quite some time. Rutherford then suggested that this shortfall must be made up by another fundamental particle. This particle has to be electrically neutral, and has to carry a mass equal to that of the proton, namely 1. He named the particle, in advance, as neutron.

The glory of discovering the neutron went to Chadwick, one of Rutherford's students. When alpha particles were made to strike a beryllium target there appeared some radiations which were highly penetrating and were capable of ejecting protons from hydrogen, helium, etc. From an analysis of the velocity, mass and charge of the radiation Chadwick concluded that the particles had the same mass as that of protons but had no charge. Consequently these were Rutherford's neutrons. The reaction is:

$$^{9}_{4}Be + ^{4}_{2}He \rightarrow ^{12}_{6}C + ^{1}_{0}n$$

where the superscripts represent the mass numbers and subscripts the atomic numbers.

An interpretation of the atomic nuclei on the basis of neutrons and protons is now a simple affair. Taking oxygen of mass number 16, for example, and recalling that the atomic number of the element is 8, we have an atomic nucleus composed of 8 protons and 8 neutrons. *Since neutrons contribute only to the mass of the element but does nothing toward charge it follows that there may exist species with the same number of protons but varying numbers of neutrons inside the nucleus. Such species must belong to the same element and must vary only in their mass numbers.* They are called *isotopes*. Thus $_1^1H, _1^2H, _1^3H$ are three isotopes of hydrogen, and $_8^{16}O, _8^{17}O$ and $_8^{18}O$ are three isotopes of oxygen.

Further informations on nuclear stability, nuclear binding forces and nuclear phenomena are given in Chapter 12.

1.2. THE EXTRANUCLEAR ELECTRONS

The nuclear region has a negligibly small dimension $\sim 10^{-13}$ cm compared to the overall atomic dimension $\sim 10^{-8}$ cm. The negatively charged region with a radius some 10^5 times as large as the nucleus is the principal area of interest to a chemist.

1.2.1. The Wave Model for Light. Newton had long back shown that sunlight could be separated, by passage through a prism, into light of many colours (red to violet), thus giving rise to a *spectrum*. A light pattern consisting of a continuous sequence of colours varying from red to violet, is called a *continuous spectrum*. On the other hand some light sources may give rise to one or a few coloured lines separated by dark spaces. This type of spectrum is called a *line spectrum*. The colour and position of a line spectrum must coincide with the position of the same colour in the continuous spectrum. It was observed by spectroscopists that atoms of various elements on excitation gave characteristic emission spectra. The emission spectra were not continuous bands of light from red to violet, such as that in sunlight; instead each excited element gave out a spectrum consisting of a number of separate lines and no two elements gave identical spectra. The line spectra are produced by atoms, and therefore these are often referred to as *atomic spectra*. Atomic spectra are usually given by outer electrons while X-ray spectra are produced both by outer and inner level electrons.

In the nineteenth century a theory of light, based on the assumption that light is a wave, was in use by scientists. A light wave must have characteristic properties, namely the wave must have energy, wave length, amplitude, velocity and frequency. Visible light was but a small part of a vast continuous spectrum of radiation that is electromagnetic in nature. Experimentally the velocity, c, of all electromagnetic radiation is found to be the same $\sim 3 \times 10^{10}$ cm/sec in a vacuum. Figure 1.7 shows a wave with its wave length and amplitude. The distance from a crest to the next crest, or from a trough to the next trough, is called

the *wave length* (λ). Amplitude is the height of the wave measured (along the *y* axis). The number of waves to pass by a given point in one second is the frequency (ν) of the wave. Since all electromagnetic waves travel with the same velocity, *c*, more waves of a shorter wave length will pass by per second than waves of longer λ. It follows that λ and ν must be connected by an inverse relation:

λ ∝ 1/ν; λν = a constant = distance covered by the wave in a second = *c* where *c* is the velocity of light, 3×10^{10} cm/sec.

Fig. 1.7. Schematic diagram showing wave length & amplitude.

There appeared two difficulties in the interpretation of the properties of light in terms of wave theory. One difficulty related to the line spectrum emitted by elements. The other difficulty was the explanation of the observation that a metal emitted electrons only when it was excited by light (photoelectric emission) of wave lengths shorter than some wave length characteristic of the metal. Thus only light of certain minimum energy could knock electrons from a given metal surface.

The explanation of these experimental observations was not possible on classical wave theory. Planck postulated a new and revolutionary theory that *radiant energy emitted by an element was not continuous in nature but, rather was emitted in discrete units, bundles or quanta.* He assumed that energy in matter was in bundles. A bundle of energy, that is, a quantum of energy emitted as light is called a photon. Planck showed that the energy of a photon was proportional to its frequency ν;

$$E \propto \nu \; ; \; E = h\nu$$

where *h* is called *Planck's constant* and has the value 1.5836×10^{-37} Kcal-sec or 6.627×10^{-27} erg-sec.

This model afforded an explanation of line spectrum given by various elements. According to quantum theory of radiation fixed wave length or frequency of the emission lines corresponds to definite, fixed energy values. When atoms are energised or excited to higher levels by heating they get rid of the extra energy by giving it off as photons and thus return to the original ground states. Atoms of different elements emit certain (but different) amounts of energy that are characteristic of the particular element. It should be realised that line spectra (atomic spectra) prove that an atom does not give off any haphazard amount of energy but only quantised amounts. There must be some clue hidden in the electronic structures of atoms that must prevent it from emitting photons of all energies.

Production of electrons in photoelectric emission is the result of the absorption of a quantum of energy by the atom. Electron emission could occur only when the energy of the photon of the exciting light is greater than some minimum energy. When light photons with sufficient energy are absorbed, one electron is emitted
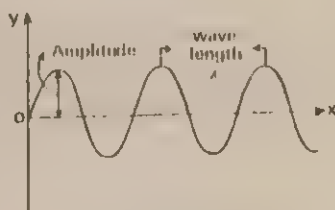
for each photon absorbed. Light quanta with too small energy cannot force electron emission and only succeeds in raising the temperature of the substance.

1.2.2. Line Spectra of Hydrogen and Bohr's Model. The emission spectrum of hydrogen atom was determined experimentally and it was possible to relate the frequencies of the different spectral lines by a simple equation:

$$\nu = R \left(\frac{1}{n_I^2} - \frac{1}{n_{II}^2} \right)$$

where n_I and n_{II} are integers and R is a constant, called the Rydberg constant after the name of the discoverer.

The existence of discrete spectral emission could hardly be explained by any model at Rydberg's time. The order and regularity of the true spectra indicated quantised emission of energy by the excited hydrogen atoms.

According to Rutherford's model the entire mass of the atom was concentrated in a tiny, positively charged nucleus around which the extranuclear electrons were moving in circular orbits. Since a stationary electron in such orbits will be dragged on to the nucleus, Rutherford had to propose that the extranuclear electrons were in constant motion in the orbit so that the electrostatic force of attraction between the electron and the nucleus was balanced by the centrifugal force tending to take the electron off the orbit.

The Rutherford model was, however, not in conformity with the classical model of electromagnetic radiation. A moving charged particle will emit radiation, will then lose kinetic energy and eventually will hit the nucleus and perish.

To resolve the anomalous position Bohr proposed several novel postulates:

1. An atom possesses several stable circular orbits in which an electron can stay. So long as an electron stays in a particular orbit there is no emission or absorption of energy.

2. An electron can jump from one orbit to another of higher energy on absorption of energy, or from one orbit to another of lower energy with emission of energy.

3. The angular momentum of an electron moving in an orbit is an integral multiple of $h/2\pi$.

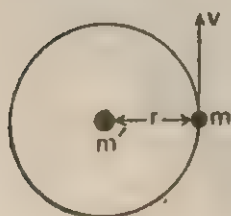Bohr's model is shown in Fig. 1.8. The nucleus has a mass m' and the electron a mass m. The radius of the circular orbit is denoted by r and the linear velocity of the electron by v. In order that the orbit be stable, the centrifugal force exerted by the moving electron must equal the attractive forces between the nucleus and the electron. Two attractive forces are in operation—one being the electric force of attraction between the nucleus (proton) and the electron, the other being the gravitational force of attraction. However the gravitational force is comparatively weak and can be neglected.

FIG. 1.8. Bohr's model of the hydrogen atom.

Then,

centrifugal force $= \dfrac{mv^2}{r}$; electric force of attraction $= \dfrac{e^2}{r^2}$

and $\dfrac{mv^2}{r} = \dfrac{e^2}{r^2}$; $\therefore \dfrac{e^2}{r} = mv^2$ ...(1)

The energy of an electron moving in one such Bohr orbit can now be calculated remembering that the total energy is the sum of the kinetic energy T and the potential energy V. Thus:

$T = \frac{1}{2} mv^2$ and V is the energy due to electric attraction and is given by:

$$V = \int_{\infty}^{r} \frac{e^2}{r^2} dr = -\frac{e^2}{r}$$ ...(2)

Thus the total energy $E = \frac{1}{2}mv^2 - \dfrac{e^2}{r} = \frac{1}{2}mv^2 - mv^2$

$$= -\tfrac{1}{2}mv^2 = -\tfrac{1}{2}\frac{e^2}{r}$$ ....(3)

The energy can thus be calculated provided we know the value of r. If r is varied from zero to infinity all energies will be allowed. If this were the case the spectrum of hydrogen atom would have been a continuous spectrum instead of a line spectrum.

Now *Bohr made a remarkable suggestion that the angular momentum of the system, equal to mvr, can assume only certain definite values or quanta. The result follows immediately—instead of all possible r values only certain definite r values are permitted. Thus only certain, definite orbits are available to the revolving electron.* According to Bohr's theory the quantum unit of angular momentum is $h/2\pi$ (h being Planck's constant):

$$mvr = n\,\frac{h}{2\pi}$$ ...(4)

where n can have values 1, 2, 3 ... ∞. The v is given by:

$$v = n\,\frac{h}{2\pi}\cdot\frac{1}{mr}$$

Then $\dfrac{e^2}{r} = mv^2 = \dfrac{mn^2h^2}{4\pi^2 m^2 r^2} = \dfrac{n^2 h^2}{4\pi^2 m r^2}$ ...(5)

and $r = \dfrac{n^2 h^2}{4\pi^2 m e^2} = n^2 \cdot a_0$ where $a_0 = \dfrac{h^2}{4\pi^2 m e^2}$ ...(6)

We thus have a solution for the radius of the permitted electron orbits in terms of the *quantum number* n. Taking $n = 1$, the radius of the first stationary orbit is:

$$r = \frac{1.h^2}{4\pi^2 m e^2} = 1.\frac{(6.627 \times 10^{-27}\ \text{erg-sec})^2}{4(3.1416)^2\,(9.108 \times 10^{-28}\ \text{gm})\,(4.8 \times 10^{-10}\ \text{esu})^2}$$

$$= 0.529 \times 10^{-8}\ \text{cm} = 0.529\ A^\circ = a_0 \ldots (1A^\circ = 10^{-8}\ \text{cm})$$

2

The radius of the second ($n = 2$) orbit will be $4a_0$, that of the third ($n = 3$) will be $9a_0$ etc. The energy associated with the permitted orbits is given by:

$$E = -\tfrac{1}{2}\frac{e^2}{r} = -\frac{2\pi^2 m e^4}{n^2 h^2} = \frac{E_{(n=1)}}{n^2} \qquad \dots(7)$$

the energy being governed by the value of the quantum number n.

As n increases the energy becomes less negative and hence the system becomes less stable. Also note that with increasing n, the radius, r, also increases. Thus increasing r also makes the orbit less stable.

The explanation of the Rydberg equation is now simple. The most stable orbit must be the one with the lowest energy (ground state). Equation (7) shows that the lowest energy state is the one with $n = 1$. States with $n > 1$ are the higher energy excited states. Provided the right amount of energy is supplied the electron may jump from $n = 1$ to another higher level. Conversely energy will be released in the form of light of definite frequency when the excited electron returns to its ground state. Since energy and frequency of the emitted light are connected by Planck relation

$$E = h\nu$$

it follows that

$$\bar{\nu} = \frac{E}{h}$$

The energy corresponding to a particular line in the emission spectrum of hydrogen atom is the energy difference between an initial state I and a final state II, so that

$$E = E_{II} - E_I$$

$$= -\frac{2\pi^2 m e^4}{n_{II}^2 h^2} - \left(-\frac{2\pi^2 m e^4}{n_I^2 h^2} \right)$$

$$= \frac{2\pi^2 m e^4}{h^2}\left(\frac{1}{n_I^2} - \frac{1}{n_{II}^2} \right) \qquad \dots(8)$$

Then ν corresponding to the energy E is given by:

$$\nu = \frac{E}{h} = \frac{2\pi^2 m e^4}{h^3}\left(\frac{1}{n_I^2} - \frac{1}{n_{II}^2} \right) = R\left(\frac{1}{n_I^2} - \frac{1}{n_{II}^2} \right) \qquad \dots(9)$$

where R is the Rydberg constant.

This relation tells us that as we go to higher and still higher orbits the energy gap between two immediate orbits continues to decrease.

Putting $n = 1$, $n = 2$, $n = 3$ etc in equation (7) we get the energies of the different stationary states for the hydrogen electron. The transition energies can all be calculated from the above relation (9). Fortunately the experimental spectra of hydrogen atom also exhibited several series of lines (Fig. 1.9). Transitions to the ground state ($n = 1$) from $n = 2$, $n = 3$, $n = 4$, etc excited states constitute the

Lyman series in the ultraviolet region. Transitions to the $n = 2$ level from the other excited levels ($n > 2$) constitute the *Balmer series* in the visible. Shifts of electrons
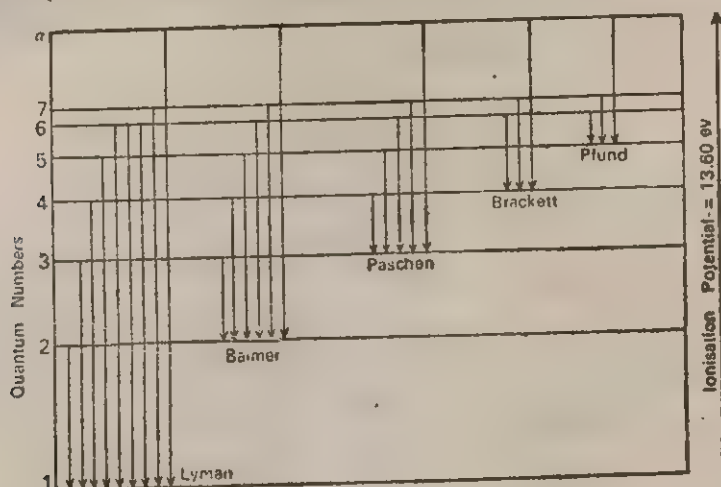

FIG. 1.9. Emission spectra of hydrogen atom.

from excited levels to the $n = 3$ level give the *Paschen series* in the infrared. The energy corresponding to the transition from $n = \infty$ to $n = 1$ obviously gives the ionisation potential (Chapter 4) of the hydrogen atom:

Ionisation potential of the hydrogen atom

$$= E_H = \frac{2\pi^2 me^4}{h^2}\left(\frac{1}{1^2}-0\right)$$

$$= 2.179 \times 10^{-11}\ \text{erg}$$

$$= 2.179 \times 10^{-11} \times 6.2419 \times 10^{11} ev$$

$$= 13.60 ev$$

Note that $-E_H = E_{(n=1)} =$ energy of the ground state. The energies of the excited states are :

for $n = 2;\ -13.6/2^2 = -3.4 ev$

$n = 3;\ -13.6/3^2 = -1.51\ ev$ etc.

Using the value of 9.108×10^{-28} gm for the mass of the electron, the Bohr theory predicts the following value of the Rydberg constant:

$$R = \frac{2\pi^2 me^4}{h^3} = \frac{2(3.1416)^2\,(9.108 \times 10^{-28}\ \text{gm})\,(4.8 \times 10^{-10}\ \text{esu})^4}{(6.627 \times 10^{-27}\ \text{erg-sec})^3}$$

$$= 3.2898 \times 10^{15}\ \text{cycles/sec}$$

It is a common practice to evaluate R in terms of wave numbers $\bar{\nu}$ instead of in frequency. Wave number and frequency are connected:

$$\lambda \nu = c;\quad \nu = \frac{c}{\lambda} = c\bar{\nu}\ \text{so that}\ \bar{\nu} = \frac{\nu}{c}$$

where c is the velocity of light. Recall that frequency, v, indicates the number of waves passing a given point per second and is expressed as cycles per second. Wave number, $\bar{v}$, on the other hand stands 'for the number of waves contained in unit length i.e. per centimetre (cm^{-1}).

Thus $$R = \frac{3.2898 \times 10^{15} \text{ cycles/sec}}{2.9979 \times 10^{10} \text{ cm/sec}} = 109{,}737 \text{ cm}^{-1}$$

The experimental value for R is 109,677 cm^{-1} showing a remarkable agreement between experiment and Bohr's theory.

If we consider a general case of an electron moving about a nucleus of charge $+ Ze$, equation (1) will take the form:

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2}$$

Equation (5) will then reduce to:

$$\frac{Ze^2}{r} = mv^2 = \frac{n^2 h^2}{4\pi^2 m r^2} \text{ whence } r = \frac{n^2 h^2}{4\pi^2 m Z e^2}$$

$$\therefore \quad E = -\tfrac{1}{2}\frac{Ze^2}{r} = -\tfrac{1}{2}\frac{Ze^2.4\pi^2 m Z e^2}{n^2 h^2} = -\frac{2\pi^2 m Z^2 e^4}{n^2 h^2}$$

As Z increases (maintaining the same n) E becomes more negative and thus the system becomes more stable. Also note that n remaining the same r decreases with increasing Z.

Equation (8) will now be of the following form:

$$E = E_{II} - E_I = \frac{2\pi^2 Z^2 m e^4}{h^2}\left(\frac{1}{n_I^2} - \frac{1}{n_{II}^2}\right)$$

The reader can easily conclude that the Rydberg constant of helium atom ($Z = 2$) will be four times as large as that of the hydrogen atom ($Z = 1$).

From the above relation it is possible to arrive at the results of Moseley. For given n_I and n_{II} we can write:

$$h v = E = E_{II} - E_I = \frac{2\pi^2 m e^4}{h^2}\left[\frac{1}{n_I^2} - \frac{1}{n_{II}^2}\right] Z^2$$

$$\therefore v = \frac{2\pi^2 m e^4}{h^3}\left[\frac{1}{n_I^2} - \frac{1}{n_{II}^2}\right] Z^2$$

In a multielectron atom of nuclear charge Z the outer electrons will feel a diminished force field $Z_{effective}$ ($= Z - \sigma$) where σ is the screening constant.

$$\therefore v = \frac{2\pi^2 m e^4}{h^3}\left[\frac{1}{n_I^2} - \frac{1}{n_{II}^2}\right](Z - \sigma)^2$$

For a given radiation n_I and n_{II} are constant.

$$\therefore \sqrt{v} = \text{constant } (Z - \sigma) = a\,(Z - \sigma)$$

Bohr's model indicated that certain, definite electronic levels are only permitted. These levels are called stationary states. The electron is not permitted to stay anywhere in between these permitted orbits. The situation may be likened to a man's climbing or descending a ladder. A ladder has a certain number of definite rungs which can serve as the man's foothold. The man has to have his foothold on one of these permitted rungs. He cannot stand in between these rungs. Thus a man's movement along a ladder (or say a staircase) produces a quantized set of upward or downward jumps and thus can be likened to the line spectrum of the excited hydrogen atom. Quantitatively speaking the analogy is not a happy one. Whereas in ladders or along a staircase the gap between two consecutive steps is commonly the same, for electron orbits the energy difference between consecutive levels is different, and in fact gets smaller as the energy of the levels increases.

Merits and Demerits of Bohr's theory. Bohr's theory successfully explained the spectra of simple one-electron hydrogenic systems like H, He^+, Li^{2+}, etc. The theory predicted electronic transitions which were in close agreement with those obtained experimentally by Rydberg. The radius of the first Bohr orbit of the hydrogen electron was also in agreement with the most probable radius of the ground state predicted by Schrödinger's wave model. However the theory failed in more complicated many-electron systems. It also failed to explain the complicated spectra obtained in a magnetic field. Furthermore by precisely stating the radius of the orbits the theory was in conflict with Heisenberg's uncertainty principle which states that for extremely small subatomic particles it is not possible to be simultaneously precise about their position and momentum.

1.2.3. The Quantum Numbers and Sommerfeld's Modification of Bohr's Model.

Bohr introduced a principal quantum number n, on the value of which the energy of transition of the electron from one circular orbit to another depended. As the value of n increases so does r. *The principal quantum number describes the size of the orbits.* With the advent of sensitive spectrometers it was observed that what was originally considered to be a single line in the hydrogen spectrum was really composed of several closely spaced lines. This meant that there must be several close energy levels rather than a single level for each quantum number n. The failure of the Bohr model for line spectra of multielectron atoms led Sommerfeld to consider that besides circular orbits there may be possible also elliptical orbits. To describe elliptical orbits more than one quantum number appeared necessary.

For circular orbits the radius r remains the same while the electron completes a rotation (0° to 360°) about the nucleus. For an elliptical orbit, however, the radius r varies. Thus for circular motion only the angle of revolution varies but for elliptical motion both the angle and the radius vary. Sommerfeld, therefore, introduced a second quantum number k which could have values from 1 up to n. Sommerfeld brought in a more general postulate that for the stationary states the so-called *action integral* $\oint p_i \, dq_i$ over one period of motion has to be an integral multiple of h:

$$\oint p_i \, dq_i = n_i h$$

where n_t is a whole number, p_t any generalised momentum which depends on the corresponding coordinate q_t. When dq_t is equal to $d\phi$ (ϕ being the angle of rotation) p_t is equal to p_ϕ, the angular momentum of the system. Classical mechanics tells us that the angular momentum of an isolated system is a constant. So we can write:

$$\oint p_\phi \, d\phi = p_\phi \int_0^{2\pi} d\phi = 2\pi p_\phi = n \; h$$

so that $p_\phi = n_\phi \dfrac{h}{2\pi}$ i.e. as with Bohr postulate the angular momen-

tum is an integral multiple of $h/2\pi$. But for an elliptical orbit r is not a constant and hence we have a further condition:

$$\oint p_r \, dr = n_r \, h$$

where p_r is the linear momentum in the direction of r. n_r is the radial quantum number and n_ϕ is called the azimuthal quantum number k. Sommerfeld demonstrated that the energy of the electron depends on the principal quantum number n which was defined as: $n = k + n_r$. While n stood for the major axis of the elliptical orbit k stood for the minor axis. It follows that when $k = n$ the orbit becomes circular. This new quantum number k has since been replaced by l called the azimuthal quantum number such that l can have integral values from 0 to $(n-1)$. Thus l is $(k-1)$. The angular momentum of the electron due to its orbital motion is given by:

$$mvr = \sqrt{l(l+1)} \frac{h}{2\pi}$$

Since l is responsible for the ellipticity of the orbits, l values describe the shape of the electron orbits.
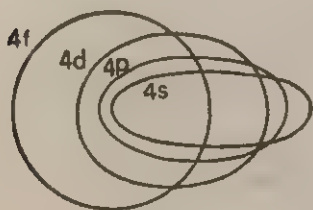

FIG. 1.10. Bohr-Sommerfeld orbits with $n = 4$, and $l = 0(s)$, $1(p)$, $2(d)$, $3(f)$.

Electrons with $l = 0, 1, 2, 3$ are called s, p, d and f electrons and the corresponding levels are called s, p, d and f sublevels or subshells. When $l = 0$ angular momentum is zero. These are s electrons with the most eccentric elliptical orbits (Fig. 1.10). s electrons are closest to the nucleus, are held more firmly and are of lower energy than electrons with higher l values. When $l = n-1$ the orbits become circular. *Therefore orbits with increasing values of l are also orbits of increasing energy.*

Zeeman had noticed that line spectra became more complicated on application of a magnetic field. This could be explained by further elaborating the azimuthal quantum number. It was necessary to postulate that the angular momentum of the electron in the direction of the magnetic field was given by $m_l \, h/2\pi$ where m_l is an additional quantum number designated as *magnetic quantum number*.

Since the line spectra were split further in a magnetic field it was concluded that the magnetic quantum number can assume only certain permitted values. These are given by

$$m_l = +l, (l-1) \ldots 0 \ldots -(l-1), -l,$$

a total of $2l + 1$ values. If the orbital angular momentum is represented by a vector l (where $l = \sqrt{l(l+1)} \dfrac{h}{2\pi}$, l being the azimuthal quantum number), then the vector can assume $2l + 1$ orientations in a magnetic field (Fig. 1.11). The components of l in different orientations along the direction of the applied magnetic field represents the different m_l values. For $l = 2$ we have five different orientations possible for the orbit in a magnetic field since m_l can have values $+2, +1, 0, -1$ and -2. These five orientations of the orbit are shown in Fig. 1.11. The direction of the vector is the direction to which the forefinger points while the thumb describes a progressing right handed screw motion, the motion being that of the moving body. Note when the plane of rotation of the electron is perpendicular to the field direction, the length of the component of the vector l along the field direction is equal to l. Thus m_l values indicate the tilts of the orbits with respect to the field direction. Positive m_l values indicate components of l along the field direction and negative values stand for components opposite to the field direction.
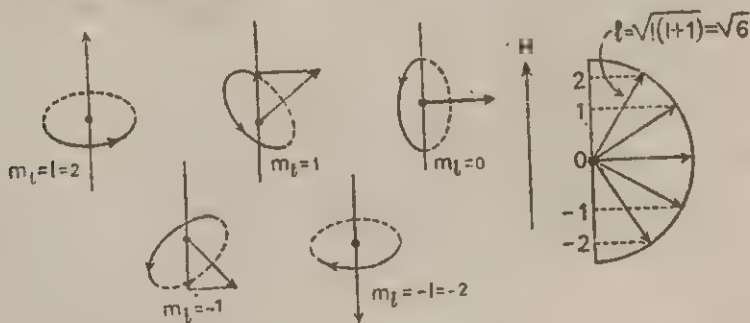

FIG. 1.11. Tilts of orbital planes and magnetic quantum numbers.

Besides the three quantum numbers n, l and m_l a fourth quantum number, namely *spin quantum number*, was necessary to completely describe an electron in a particular shell. The electron itself can be regarded as a small magnet. A beam of hydrogen atoms can be split into two beams by a strong magnetic field. This indicates that there are two kinds of hydrogen atoms which can be differentiated on the basis of their behaviour in a magnetic field. It has been postulated that each electron spins around its own axis like a top and thereby behaves like a small magnet. A spinning electron can have only two possibilities. The electron can either spin clockwise or counterclockwise (Fig. 1.12). The two directions of spin are represented by arrows pointing either up or down (↑ or ↓). This fourth quantum number, s, is independent of the other three quantum numbers n, l or m_l.

's' can have two possible values $+\frac{1}{2}$ or $-\frac{1}{2}$ depending on the direction of rotation of the electron about its axis. This spin angular momentum is given by:
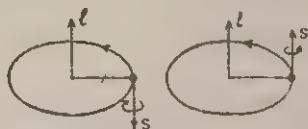
$$\sqrt{s(s+1)}\ h/2\pi$$

FIG. 1.12. Two directions of spin of an electron

With these four quantum numbers it is possible to proceed with the building up of the electronic structure in multielectron systems. But we will defer that till we describe the currently followed probability model of the electron.

1.2.4. Duality of Matter, Uncertainty Principle and the Failure of Bohr Model.
The inadequacy of Bohr's theory was revealed by finer experimental details of multielectron system and the theory was in contradiction to Heisenberg's uncertainty principle. Soon de Broglie, Heisenberg and Schrödinger made lasting contributions in this area and Bohr's theory based on the particle nature of the electron was replaced by a wave model.

Thomson's studies had revealed the particle nature of the electron, namely that it has a mass, energy and a momentum. *de Broglie pointed out that just as light has both particle and wave nature, so also is the case with electrons. He suggested that electrons travel in waves, analogous to light waves.* His idea could be fitted to derive the same relation that Bohr arrived at from his particle treatment of the electron.

The mass of a photon, the smallest light quanta, is given by the famous mass-energy equivalence equation of Einstein:

$$E = mc^2$$

Recalling that $\qquad E = h\nu \qquad$ we have $m = \dfrac{h\nu}{c^2}$ ... (10)

The momentum p of a photon is $p = mv = mc$ so that $p = \dfrac{h\nu}{c}$ ... (11)

Since frequency ν, wave length λ and velocity v of the photon are connected as:

$$\lambda = \frac{v}{\nu} = \frac{c}{\nu}$$

we have from (11) $\qquad \lambda = \dfrac{c}{\nu} = \dfrac{h}{p}$ ... (12)

Our combining the Einstein equation and the Planck equation is a recognition of the dual nature of light.

The above equation (12) gives the wave length of the light waves and also of electron waves, provided electrons can be considered to generate waves. This

relation states that there must be a wave associated with the particle. In order to connect this with the Bohr's model, there must be an integral number of wave length that would just fit into the circular orbits of Bohr. Such integral number of wave lengths would generate a standing wave instead of a stationary Bohr orbit (Fig. 1.13). *A standing wave produces a stationary pattern, its profile being fixed within the space allowed to it. It does not travel beyond the allowed space.* Then we have:

$$n\lambda = 2\pi r$$

where λ is the wave length of the standing wave, n is an integer and r the radius of the Bohr orbit. Substituting for λ from (12) we get

$$n\left(\frac{h}{p}\right) = 2\pi r \text{ or } n\left(\frac{h}{2\pi}\right) = rp = mvr$$

$$= \text{angular momentum} \qquad \ldots (13)$$

Thus de Broglie waves can be used to explain the Bohr model.

Bohr Orbit
n=5

FIG. 1.13. A standing wave with $n = 5$

Within a few years of de Broglie suggestion, Davisson and Germer tested de Broglie's predictions by diffracting electrons by crystals, the diffraction being similar to the diffraction of X-rays. They thus established that a beam of electrons did really possess wave properties and that the wave length to be associated with electrons of known p ($= mv$) value was exactly that predicted by the de Broglie equation:

$$\lambda = \frac{h}{p}$$

de Broglie relationship is applicable to all particles but for heavy particles the wave length is too small to be observed experimentally.

The dual nature of the electron led Heisenberg to propose his uncertainty principle. The principle states that it is impossible to know accurately both of the two important factors which determine the movement of an electron—its position and velocity (or momentum). Detection of a particle as tiny as the electron requires very low wave length (high energy) radiation. The electron being very small, collision with a high energy photon changes the momentum of the electron. Therefore, even if we could accurately measure the position of the electron we could not simultaneously measure its momentum as precisely because the probing photon would invariably change its momentum. This change in momentum is due to what is known as *Compton effect*. Compton has shown that when X-rays, which consist of waves of energy $h\nu$, fall on carbon the scattered radiation contains some rays of longer wave length. Alongwith the scattering, the electron also suffers a simultaneous recoil. The scattering, in fact, results from an interaction of the X-rays with the electrons of the carbon
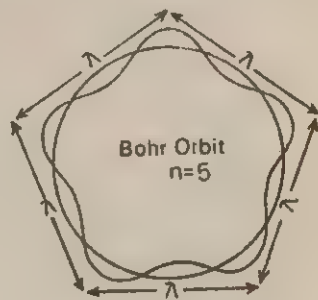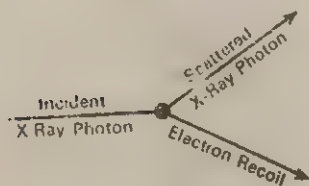

Fig. 1.14. Compton effect

atom. Compton could explain mathematically the increase in the wave length of the scattered X-rays as also for the recoil of the electron by treating the collisions as though these had originated from two rigid spheres. If $\triangle p$ and $\triangle q$ are the uncertainties in the measurement of p (momentum) and q (position) of the electron then the product $\triangle p$. $\triangle q$ will be of the order of h, the Planck's constant. This can be seen from the following considerations:
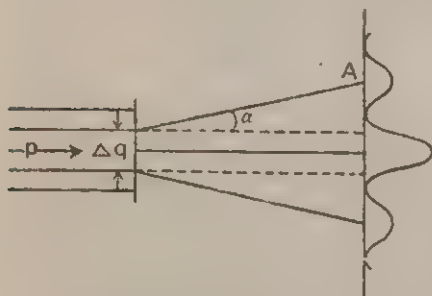

Fig. 1.15. Diffraction of electron wave at a slit (uncertainty principle)

Consider an electron wave moving with a momentum p passing through a slit of width $\triangle q$ and hitting a screen. The passage of the electron through the slit is totally uncertain.

Let us assume that the electron moves out of the slit at an angle a with its original direction and hits the screen at some point A (Fig 1.15) above its original direction. In the process it gains an additional momentum in the vertical direction i.e. $\triangle p = p \sin a$. Angle a, according to diffraction theory, is given by $\lambda / \triangle q$. Then $\triangle p = p \sin a = p \sin \lambda / \triangle q \simeq p \ \lambda / \triangle q$. But $p = h/\lambda$ so that $\triangle p = h / \triangle q$ i.e. $\triangle p$. $\triangle q \simeq h$.

Thus the uncertainty principle tells us that it is not possible to think of the electron moving around a nucleus from one point to another with a fixed velocity at each point. We are, therefore, to consider the electron as having a definite probability of being discovered at each point in space. The uncertainty principle also leads us to the conclusion that experiments will not allow us to decide exactly whether the electron is a particle or a wave. *We have to regard the electron both as a particle and as a wave.* For some purposes we may consider the electron as a particle and for some other purposes it has to be considered as a wave. Particle nature and wave nature of the electron are, therefore, complementary to each other.

It may be recalled that the radius of the first stationary orbit in Bohr's model of the hydrogen atom is 0.529 Å. The electron in the ground state rotates about the nucleus at a distance of precisely 0.529 Å at all times. Bohr's theory thus shows that we know precisely both the energy (also velocity) and the position (radius) of the electron. According to Heisenberg such precise informations cannot be available for so small a particle as the electron. The conflict can be removed only if we have a model that will tell us precisely about the energy of the electron but will leave an uncertainty about its position.

1.2.5. The Wave Model of the Electron. The need of the hour was to develop an atomic model which will explain the stationary electron energy states (the line spectra) and at the same time will not violate the uncertainty principle. Schrödinger set up an equation that treated the electron as a wave, and that yielded solutions only for certain energy values of the electron. Thus certain stationary energy states were recognised. This equation also allowed calculation of the

probability of discovering the electron at a particular time at a particular point. Thus whereas Bohr's theory of the hydrogen atom says that 0.529 Å is the radius of the ground state electron orbit, Schrödinger's model predicts that 0.529 Å is the most probable distance from the nucleus where the electron in the ground state may be found. The model further says that the electron may be found at distances both shorter and longer than 0.529 Å although the probability is less than at 0.529 Å.

A somewhat elaborate discussion on Schrödinger's equation appears in Appendix. In this chapter we continue the discussion in a non-mathematical way. Since an electron has a wave character, it is described by a wave amplitude commonly called wave function Ψ. The wave function can assume positive, negative or imaginary values but Ψ^2 will always be positive and real. The square of the value of Ψ at any point gives the probability density of the electron at that point. Instead of considering only a point if we take a volume element, then probability of finding an electron in that volume element in space is the square of the value of Ψ, multiplied by that volume element of space. For conceptual aid the point is elaborated further.

With light waves the intensity is proportional to the square of amplitude Ψ, that is to Ψ^2. Then Ψ^2 is proportional to the number of photons reaching per unit volume containing a particular point per unit time. In Fig 1.16 the height A multiplied by R is proportional to the frequency of photon arrival in the region R. A more reasonable interpretation is that A represents the probability of finding a photon at this point. It can be guessed that this probability will be higher the larger the area R is. Thus the probability is Ψ^2 multiplied by

FIG. 1.16. A probability interpretation.

R. When we consider three dimensions R will represent the volume element as stated above. Note that Ψ^2 *alone will represent the probability per unit volume or the probability density.*
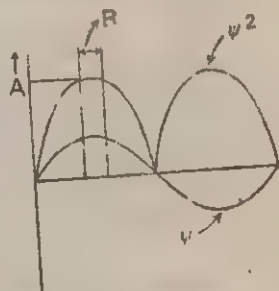
According to Schrödinger, the position of an electron cannot be exactly specified. We can only talk of its probability of being found at a time at a point. This probability is expressed in the form of an orbital instead of an orbit. *An orbital is a region in space where there is a high probability of finding an electron.*

1.2.6. Orbitals and the Quantum Numbers. A wave function Ψ representing an electron is the product of two parts: a radial part and an angular part. The square of the radial part of the wave function indicates the probability of finding the electron at any distance r from the nucleus. The square of the angular part of the wave function gives the probability of finding an electron in a particular direction from the nucleus. The radial dependence and the angular dependence of the wave function taken together tell us that a three dimensional standing electron wave (orbital) can be pictured to have a size, a shape and an orientation.

In order to describe the size, shape and orientation of an orbital three quantum
numbers are necessary. These quantum numbers are designated by n, the *principal
quantum number*, l the *orbital angular momentum quantum number* (or *azimuthal
quantum number*) and m_l the *magnetic quantum number*. In what follows there will
be some repititions of our earlier discussion on the quantum numbers on Bohr-
Sommerfeld models but we will deliberately proceed with the repitition.

The principal quantum number n is of primary importance in determining
the size and hence the energy of the electron. For the hydrogen atom we have
already seen that the energy is fixed by the value of n. In other multielectron
atoms, the energy of each electron is dependent mostly (though not entirely) on
the value of the principal quantum number of the electron. As the value of n
increases the radius (nucleus—electron separation) increases, that is, the size of
the orbital increases. The energy also is raised. n is always integral and can assume
the values 1, 2, 3, 4, ... ∞ but not zero.

The general geometric shape of the electron wave (orbital) is described by the
second quantum number l. This quantum number is related to n for the electron
in that state thus:

$$l = 0, 1, 2 \ldots (n-1)$$

Therefore an electron with a principal quantum number n can assume 0 to $(n-1)$,
that is, n different l values. So when $n = 1$, only $l = 0$ is possible and hence only
one orbital shape is permitted. With $n = 2$, l can have two values 0 and 1 and
hence orbitals of two different shapes will be permitted and so on. These shapes
are expressed by different symbols s ($l = 0$), $p(l = 1)$, $d(l = 2)$ and f ($l = 3$) etc:

Principal Quantum Number (n)	Orbital angular momentum quantum number (l)
1	1s
2	2s, 2p
3	3s, 3p, 3d
4	4s, 4p, 4d, 4f

The third quantum number m_l is associated with the orientation of the electron
wave with respect to a given direction, usually that of a strong magnetic field.
This quantum number has no effect on the shape of the orbital or on the energy
of the electron. For a given value of l, m_l can have any integral value between
$+ l$ and $-l$, so that

$$m_l = +l, l-1, l-2, \ldots 0 \ldots -1, -2 \ldots -l.$$

With $l = 1$, m_l can assume values $+ 1, 0$ and -1 so that a p wave can have three
orientations. These three orientations are expressed by subscripts added to p as
p_x, p_y and p_z. Since an s wave has $l = 0$, its $m_l = 0$ which means that an s type
orbital has just one orientation in space. A d-type electron wave with $l = 2$ can
have five m_l values $+ 2, +1, 0, -1$ and -2 so that there are five different orienta-
tions in space. These are represented by the following notations:

$$d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2} \text{ and } d_{z^2}$$

The significance of these symbols will be evident when we take up the shapes of the orbitals.

The fourth quantum number, *spin quantum number*, has already been discussed.

1.2.7. The Shapes of Orbitals. The probability of finding an electron in space around the nucleus involves two aspects: radial probability and angular probability. It is not possible to represent completely in one diagram on paper the directional properties of electron orbitals. Two separate representations (1) a radial probability distribution and (2) an angular probability distribution must be combined mentally to have an overall shape of the orbitals.

The wave equation is written in terms of spherical polar coordinates r, θ and ϕ which are coordinates related to the Cartesian coordinates x, y and z (see Appendix 1). Then the wave function Ψ can be written as:

$$\Psi = R_{(r)} \theta_{(\theta)} \Phi_{(\phi)}$$

Thus Ψ has a radial part $R(r)$, a function only of r and an angular part $\theta_{(\theta)} \Phi_{(\phi)}$, a function of angles θ and ϕ.

Let us consider the space around the nucleus to be made up of a large number of thin concentric shells, of thickness $\triangle r$, at a distance r from the nucleus. Then the volume of such spherical shell is $4\pi r^2 \triangle r$ and the probability of finding the electron within such shell is $4\pi r^2 \triangle r \Psi_r^2$ (Ψr = radial part of the wave function). A plot of $4\pi r^2 \Psi_r^2$ against r indicates the probability of finding the electron in a
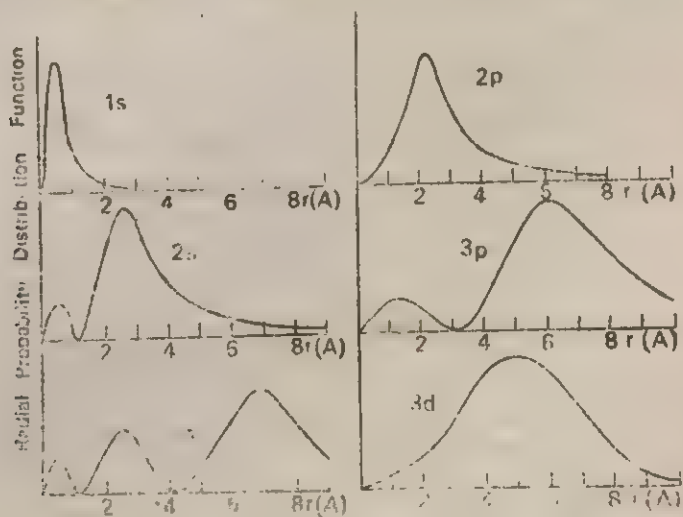

FIG. 1.17. The radial probability distribution functions for 1s, 2s, 3s, 2p, 3p, and 3d orbitals.

spherical shell of thickness $\triangle r$ at a distance r from the nucleus. $4\pi r^2 \Psi^2$ is *called the radial probability density function or radial probability distribution function.* Fig. 11.7 gives the radial probability density plots for 1s, 2s, 2p, 3p and 3d

type orbitals. Several points emerge from these plots. (1) The probability distribution is zero at the origin, the nucleus. (2) The distributions vary according to the principal quantum number, so that the larger the value of n is, the farther out the electron is likely to be from the nucleus. (3) The maximum for 1s radial distribution occurs at 0.529 Å in agreement with Bohr's calculation for circular orbit with the electron in the ground state. (4) For 2s and 3s orbitals there are two, and three maxima in the plots. For the 2s orbital the maximum probability occurs at 2.6 Å, although there is another small but definite maximum at 0.529 Å as well. For the 3s orbital the maximum occurs at 6.9 Å with two other small but definite maxima at 2.6 Å and 0.529 Å.

The angular probability distributions are of greater interest and importance. An s electron has no angular dependence because the relevant wave function is
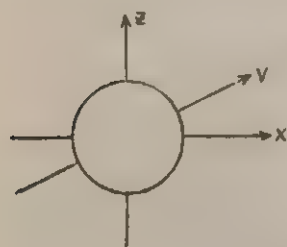

Fig. 1.18. The angular probability distribution of an s orbital.

independent of the angles θ and ϕ. There is, therefore, an equal chance of discovering the electron in any direction from the nucleus. A graphical representation of this dependence is shown in Fig. 1.18. With the nucleus at the origin of the Cartesian axes, the sphere of radius r represents the probability of finding the s electron. An s electron has a spherically symmetrical probability distribution.

As for p orbitals it has earlier been shown that there are three possible orientations p_x, p_y and p_z. The orientations of the orbital plane corresponding to $m_l = +1, 0, -1$ (Fig. 1.11) are mutually at right angles. So the orbitals designated p_x, p_y and p_z are mutually perpendicular and they are concentrated along the respective coordinate axes x, y and z. Unlike the s orbitals the angular part of the p wave functions is dependent on θ and ϕ.
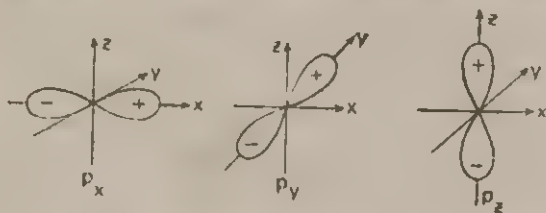
Fig. 1.19. Angular probability distribution of p orbitals.
(sign of the wave function shown)

The angular probability distributions are shaped like pears along the x, y and z axes as shown in Fig. 1.19. Thus in the p_x orbital it is most likely that the electron will be found in the direction of the x-axis. There is no probability of its being found along y and z axes. Similar results are obtained for the p_y and the p_z orbitals. The pictorial representations are but two dimensional on paper. In reality the shapes are three dimensional and the real shapes are obtained on rotating the two-dimensional representation about the appropriate axis.

The angular probability distributions of the d orbitals are shown in Fig. 1.20. In d_{xy}, d_{xz}, d_{yz} the lobes are concentrated in between the appropriate coordinate
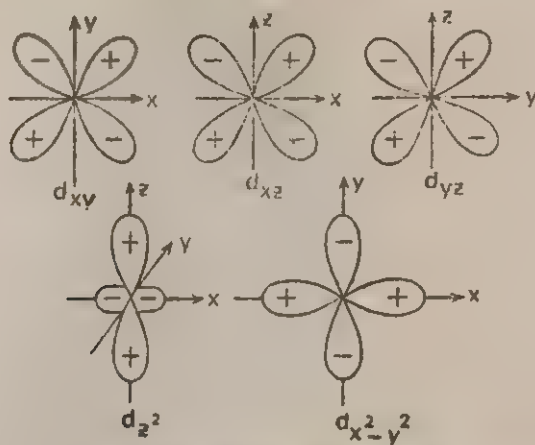

FIG. 1.20. The angular probability distribution of d orbitals.
(sign of the wave function shown)

axes. In $d_{x^2-y^2}$ the lobes lie along the x and y coordinate axes, and in d_{z^2} there are two lobes along z axis with a ring in the xy plane all around the nucleus.

In order to have a total picture of the probability of finding an electron in any orbital the radial probability distribution and the angular probability distribution must be combined. It should be noted that in two dimensions on paper it is impossible to draw the composite probability distribution. It becomes convenient, however, to think of the drawings as shapes of orbitals. Conventionally the drawing for each orbital encloses about 90% of the probability of finding the electron around the nucleus. It should be remembered that there is still one chance in ten that the electron will be located outside these orbital drawings.

It should be pointed out that for a p orbital there are two lobes along a particular axis on either side of the nucleus. The angular part of the wave function $\Psi_{(\theta,\phi)}$ has a '+' sign on one lobe and a '−' sign on the opposite lobe, although $\Psi^2_{(\theta,\phi)}$ will be positive on either side. These signs are often added on the lobes. For the d_{xy}, d_{xz}, d_{yz} and $d_{x^2-y^2}$ orbitals '+' and '−' signs occur on alternate lobes. For the d_{z^2} orbital, the two lobes on z axis carry '+' sign and the ring in the xy plane a '−' sign. These signs are very important in symmetry considerations.

1.2.8. Orbital Energy Ordering in Multielectron Atoms. Exact solutions of the Schrödinger wave equation for atoms with two or more electrons have not been possible. The orbitals of a multielectron atom are not likely to be quite the same as the hydrogen atom orbitals. For practical purposes, however, the number of orbitals and their shapes in multielectron cases may be taken to be the same as for the hydrogen orbitals. In multielectron atoms experimental studies of spectra show that orbitals with the same value of n but different l values have different

energies. The 3s orbital is of lower energy than the 3p orbitals which again are of lower energy than the 3d orbitals. However orbitals belonging to a particular type (p or d or f) will be of equal energy (degenerate) in an atom or an ion. For example the three p orbitals or the five d orbitals originating from the same n will be degenerate. We will see in Chapter 10 that the degeneracy of the five 3d
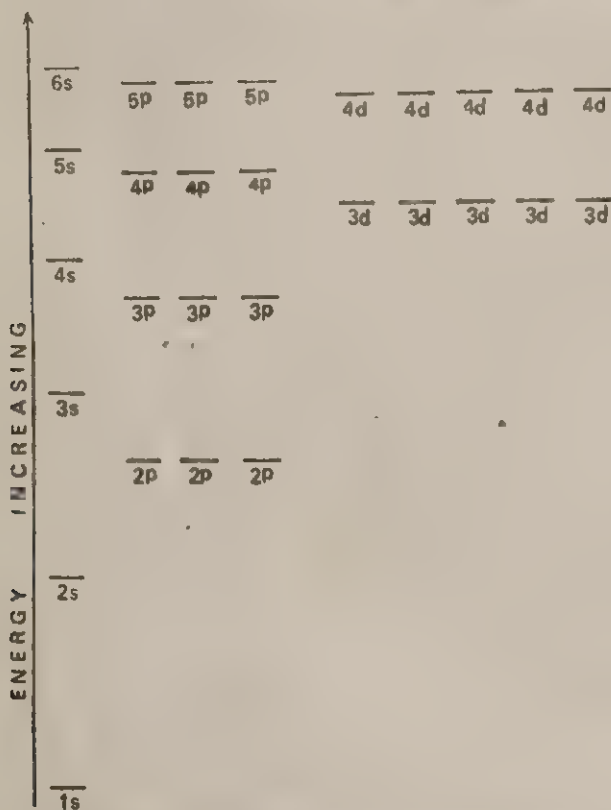
FIG. 1.21. Orbital energy diagram for multielectron atom.

orbitals may be removed in a coordination complex providing new features to spectra. The separation of the orbitals of a major energy level (a particular n) into sublevels is primarily due to the interactions among the many electrons. This interaction leads to the following relative order of the energies of each type of orbital: (Fig. 1.21). $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f \ldots$

The close proximity of the 4s and 3d orbitals (and 5s/4d; 6s/5d etc.) provides interesting properties in those multielection atoms where the d orbitals are partially occupied.

Admittedly it is often difficult for the students to remember the orbital energy diagram as shown in Fig. 1.21. A trivial but distinctly more convenient way is to make use of Fig. 1.22. The different orbitals originating from the same principal

quantum number n are written in separate horizontal lines. Now inclined parallel lines are drawn through the orbitals as shown in Fig. 1.22. Filling up of the different orbitals by electrons will follow these parallel lines. Thus the first two parallel inclined lines cover 1s and 2s orbitals so that electrons will first go to 1s and then to 2s orbitals. Thereafter will come 2p and 3s being followed by 3p and 4s but not 3d. Filling of 3d will start only after 4s. Similarly 5s orbital will be occupied before 4d. Remember, however, that the orbitals on any horizontal line are not of the same energy.

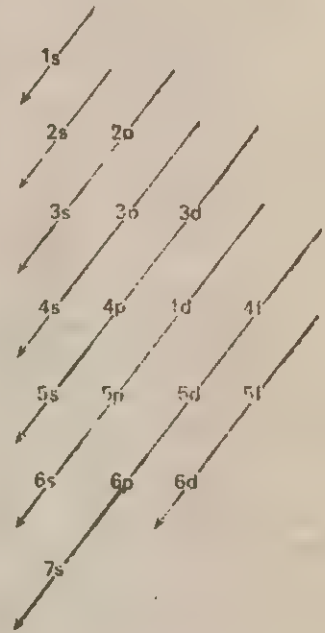**1.2.9. Multielectron Atoms: the Aufbau or Building up Principle.** The question that arises now is how many electrons can be accommodated per orbital. The answer to this follows from Pauli's exclusion principle: *no two electrons in an atom can have the same four quantum numbers.* This principle tells us that in each orbital a maximum of two electrons can be allowed. The two electrons will have the same three quantum numbers namely the same n, same l and the same m_l. Any conflict with Pauli principle can now be avoided if one of the electrons has the spin quantum number $s = +\frac{1}{2}$ and the other $s = -\frac{1}{2}$.

Fig. 1.22
Orbital occupancy order

An alternative statement of the Pauli exclusion principle is: *no more than two electrons can be placed in one and the same orbital.* When two electrons with opposite spins exist in an orbital, the electrons are said to be paired. Remembering the two-electrons-per-orbital maximum accommodation rule and recalling the number of orbitals for different n values, the following Table 1.1. can be drawn to give the maximum number of electrons admissible to different levels. The total number of electrons for a particular n is given by $2n^2$.

Table 1.1. Capacities of Electronic Levels

Principal Quantum Number, n	Number of electrons in sublevels with					Total Number of electrons $= 2n^2$
	$l = 0$	1	2	3	4	
1	2					2
2	2	6				8
3	2	6	10			18
4	2	6	10	14		32
5	2	6	10	14	18	50

Note that an s type orbital ($l = 0$) can accommodate 2 electrons, three p ($l = 1$) type orbitals a total of 6, and the five d ($l = 2$) type orbitals a total of 10 electrons and so on. Also note that the s, p, d, f, etc. orbital sets are usually called *sublevels* or *subshells*. The group of subshells (sublevels) constituting a particular n is called a *shell* or a *level*.

To determine the electronic configuration of elements the procedure is to feed electrons in different orbitals obeying certain rules. The aufbau or building up principle is based on the following rules:

1. *Electrons are fed into orbitals in order of increasing energy (increasing n) until all the electrons have been accommodated.*

2. *Electrons will tend to maintain maximum spin.* So long as vacant orbitals of similar energy are available for occupation electrons will prefer to remain unpaired. In other words electrons tend to avoid the same orbital, that is, hate to share space. This rule is known as Hund's rule of maximum spin multiplicity (see Chapter 11).

3. *Spin pairing can occur only when vacant orbitals of similar energy are not available for occupation, and when the next available vacant orbital is of a higher energy.*

Hydrogen (atomic number 1) has its only electron in the $1s$ orbital and this electronic configuration is represented as:

$$\frac{\uparrow}{1s}$$

The bar indicates the orbital and the arrow ↑ a single spinning electron in the orbital. In helium (at. no. 2) the second electron has to occupy the $1s$ orbital since the next available $2s$ orbital is of much higher energy. Obeying Pauli principle the the configuration $1s^2$ is represented as:

$$\frac{\uparrow\downarrow}{1s}$$

Lithium (at. no. 3) has the configuration $1s^2\,2s^1$, beryllium $1s^2\,2s^2$ and boron $1s^2\,2s^2\,2p^1$. After boron comes carbon and the next electron can remain unpaired in another p orbital of similar energy so that we write the configuration $1s^2\,2s^2\,2p^2$ of carbon as:

$$\frac{\uparrow\downarrow}{1s} \;\bigg|\; \frac{\uparrow\downarrow}{2s} \;\bigg|\; \frac{\uparrow}{2p} \quad \frac{\uparrow}{2p} \quad \overline{2p}$$
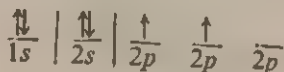
Continuing in this way we develop Table 1.2. for elements from hydrogen to neon.

Table 1.2. Electronic Configurations of Elements H to Ne

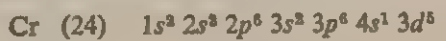| Element	Atomic Number	Electronic Configuration	Pictorial representation
H	1	$1s^1$	↑ $1s$
He	2	$1s^2$	↑↓ $1s$
Li	3	$1s^2\,2s^1$	↑↓ │ ↑ $1s$ $2s$
Be	4	$1s^2\,2s^2$	↑↓ │ ↑↓ $1s$ $2s$
B	5	$1s^2\,2s^2\,2p^1$	↑↓ │ ↑↓ │ ↑ $1s$ $2s$ $2p$
C	6	$1s^2\,2s^2\,2p^2$	↑↓ │ ↑↓ │ ↑ ↑ $1s$ $2s$ $2p$ $2p$
N	7	$1s^2\,2s^2\,2p^3$	↑↓ │ ↑↓ │ ↑ ↑ ↑ $1s$ $2s$ $2p$ $2p$ $2p$
O	8	$1s^2\,2s^2\,2p^4$	↑↓ │ ↑↓ │ ↑↓ ↑ ↑ $1s$ $2s$ $2p$ $2p$ $2p$
F	9	$1s^2\,2s^2\,2p^5$	↑↓ │ ↑↓ │ ↑↓ ↑↓ ↑ $1s$ $2s$ $2p$ $2p$ $2p$
Ne	10	$1s^2\,2s^2\,2p^6$	↑↓ │ ↑↓ │ ↑↓ ↑↓ ↑↓ $1s$ $2s$ $2p$ $2p$ $2p$

After neon the next available orbital is 3s being followed by 3p. The orbitals are then progressively filled by electrons. The elements concerned are sodium (11), magnesium (12), aluminium (13), silicon (14), phosphorus (15), sulphur (16), chlorine (17) and argon (18). Then the 4s orbital, being of lower energy than the 3d, is filled. The elements involved are potassium (19) and calcium (20):

$$K : 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 \quad \text{and} \quad Ca : 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$$

In scandium (21) the twenty first electron goes to a 3d orbital, the next available orbital of higher energy. There are five 3d orbitals with a capacity of ten electrons. From scandium to zinc these d orbitals are being filled up. *Presence of partially filled d orbitals generates some very special properties. Elements with partly filled d (or f) orbitals in elementary state or in ionic states are called transition elements.* Table 1.3 summarises the electronic configurations of the elements scandium to zinc. The configurations in Table 1.3 are given on the basis of the aufbau principle. In reality experimental studies on copper and chromium reveal that their electronic configurations are better represented as:

$$Cr \ (24) \quad 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^1\, 3d^5$$
$$Cu \ (29) \quad 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^1\, 3d^{10}$$

This reordering of electrons is due to an extra stability associated with a half filled or a filled subshell. *Strict adherence to the above definition of transition elements will exclude zinc from the list.* An elaborate discussion on these elements is reserved for Part II.

Table 1.3. Electronic Configurations of the First Series of Transition Elements

Element	Atomic Number	Electronic Configuration	Pictorial representation
Scandium	21	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$	[Ar] $\uparrow\downarrow$ (4s) | $\uparrow$ — — — — (3d)
Titanium	22	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2$	[Ar] $\uparrow\downarrow$ (4s) | $\uparrow\ \uparrow$ — — — (3d)
Vanadium	23	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$	[Ar] $\uparrow\downarrow$ (4s) | $\uparrow\ \uparrow\ \uparrow$ — — (3d)
Chromium	24	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$	[Ar] $\uparrow\downarrow$ (4s) | $\uparrow\ \uparrow\ \uparrow\ \uparrow$ — (3d)
Manganese	25	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^5$	[Ar] $\uparrow\downarrow$ (4s) | $\uparrow\ \uparrow\ \uparrow\ \uparrow\ \uparrow$ (3d)
Iron	26	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$	[Ar] $\uparrow\downarrow$ (4s) | $\uparrow\downarrow\ \uparrow\ \uparrow\ \uparrow\ \uparrow$ (3d)
Cobalt	27	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^7$	[Ar] $\uparrow\downarrow$ (4s) | $\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ \uparrow\ \uparrow$ (3d)
Nickel	28	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$	[Ar] $\uparrow\downarrow$ (4s) | $\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ \uparrow$ (3d)
Copper	29	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^9$	[Ar] $\uparrow\downarrow$ (4s) | $\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow$ (3d)
Zinc	30	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$	[Ar] $\uparrow\downarrow$ (4s) | $\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow$ (3d)

We began this chapter with a Rutherford comment. We also wish to conclude this chapter with some observations on Rutherford. Rutherford indeed did enough and left enough for the posterity. Our presentday understanding of the atomic structure had originated from the nuclear atom model of Rutherford. Much of our knowledge of the newer alchemy—artificial transmutation of elements—also came from Rutherford's brilliant experiments (Chapter 12). He began his research career under Thomson at Cambridge and later worked and taught at McGill University and then at Manchester and Cambridge. A man of prolific energy, he was awarded the Nobel Prize in 1908. What a remarkable feat he achieved in nursing and training a band of brilliant experimentalists and theoreticians of this century! Notable among them are Moseley, Soddy, Chadwick, Geiger and Bohr. All England loved and respected this man for his extraordinary contributions to human understanding. That England held Rutherford in the highest esteem

was shown on his death (1937). He was laid to rest in Westminster Abbey alongside the all-time great Isaac Newton.

STUDY QUESTIONS

1. Describe the contributions of Rutherford, Thomson and Bohr towards the elucidation of atomic structure.

2. In the line spectrum of hydrogen atom, the lines become closer and closer as the frequency is increased. Comment.

3. What are the maximum electron capacities in 3d, 4p, 4f and 5g orbitals?

4. How are the atomic number and atomic weight related to the number of protons and neutrons in the nucleus and the number of electrons outside the nucleus?

5. Describe the orbitals and spins of the electrons in the ground state of the fluorine atom.

6. Distinguish between an orbit and an orbital. Show that oxygen cannot have d-orbitals.

7. For a general case of an electron moving in an orbit around a nucleus of charge Ze show that $E = -\dfrac{2\pi^2 mZ^2 e^4}{n^2 h^2}$. Taking the ionisation potential of hydrogen as 13.6 ev calculate the ionisation potentials of the ions He$^+$, Li^{2+} and Be^{3+}.

8. A newspaper reports the discovery of an element of atomic weight between those of oxygen and fluorine but with chemical properties different from either oxygen or fluorine. Can you believe the report?

9. Write the electronic configurations for the following species and indicate which ones are isoelectronic:

$$S^{2-}, \ Cd^{2+}, \ Ne, \ Cr^{3+}, \ K^+ \text{ and } Al^{3+}$$

10. Plot a graph of the square roots of the ionisation potentials (in parentheses) versus nuclear charge for the series:

Li (5.39 ev), Be$^+$ (18.2), B^{2+}(37.9), C^{3+}(64.5). N^{4+}(97.86). Explain the observed relation and check with Chapter 4, Fig. 4.2.

11. In what respect the spectrum of He$^+$ will differ from that of H atom?

12. What are the charges (in Coulombs) associated with N^{3-}, H$^-$, Cl$^-$ and H$^+$ ions?

13. Write explanatory notes on (a) Compton effect and (b) Uncertainty Principle.

14. Present a non-mathematical and qualitative picture of the shapes of s, p and d orbitals. Which of these orbitals is the most penetrating in character?

15. Explain Pauli exclusion principle, Hund's rules and aufbau principle. Utilise these principles and rules in predicting the ground state electron distributions of the elements sodium to argon.

16. Derive a relation giving the energy of an electron moving around a proton. What is Rydberg constant? Given the Rydberg constant derive expression (or value) of the ionisation potential of hydrogen atom.

17. Cite some experimental evidence in favour of the existence of (a) atomic nucleus (b) extra-nuclear electrons and (c) isotopes.

18. Do you agree that the ground states of carbon and nitrogen atoms are as shown below?

	1s	2s	2p	2p	2p
carbon	⇅	⇅	⇅	—	—
nitrogen	⇅	⇅	⇅	↓	—
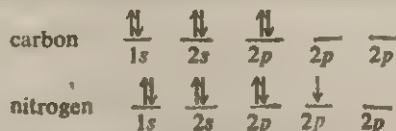
19. Explain which one of each of the following pairs is more fundamental so far as chemical properties of elements are concerned:

(a) atomic number and atomic weight

(b) protons and neutrons

20. "No more than two electrons can be placed in one and the same orbital." Is this a correct statement of Pauli exclusion principle?

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2

The Periodic Classification of the Elements

2.1. MENDELEEV'S CLASSIFICATION

Periodic classification of elements is a testimony to man's eternal quest of discovering order in nature. Today we know a good deal about the electronic structure of atoms. But in 1869 the situation was far from satisfactory. Even in 1869, handicapped by very limited informations, chemists set themselves the task of finding out if any regularity existed among the elements and their compounds. The informations available to them were restricted only to the atomic weights of the elements, density of the elements, atomic volume, melting point, boiling point and a few chemical compounds of each of the elements. Working systematically on these available informations, Mendeleev in 1869 noted that the properties of elements varied regularly with the atomic weights of the elements. Mendeleev enunciated a periodic law in the following form:

The properties of chemical elements and their compounds are periodic functions of the atomic weights of the elements.

This statement provided a new key to our understanding of the elements. Mendeleev arranged the-then known elements in horizontal rows and vertical columns such that elements of comparable properties became members of the same column. This arrangement of the elements in rows and columns is called the Periodic Table. The horizontal rows are called periods and the vertical columns called groups. Mendeleev's remarkable understanding of the problem was revealed in his leaving some vacancies in the Periodic Table for yet undiscovered elements and in his being able to predict the properties of these undiscovered elements. Gallium, scandium and germanium, for instance, were among the elements predicted by Mendeleev, and these were indeed discovered in later years. The agreement between the predicted properties and the actual properties of these elements was

astounding. The concept of periodicity of the properties of the elements and their compounds had, thus, a fine start.

Lothar Meyer, a contemporary of Mendeleev, also sought to establish a relation between the properties of chemical elements and their compounds, and atomic weights. He showed that atomic volumes of solid elements (volume in millilitres occupied by one mole of atoms of an element in solid form = gram atomic weight/density) were periodic functions of atomic weights. Readily fusible elements like the alkalies occurred on the maxima and on the ascending part of the plot of atomic volume against atomic weight. Unfortunately Lothar Meyer's work did not go a long way to establish a useful classification of elements.

2.2. MODIFICATION OF MENDELEEV'S TABLE

Mendeleev's statement of the periodic law needed to be changed in view of Moseley's researches. It may be recalled (Chapter 1) that Moseley studied the effect of cathode rays on different metal (or suitable compound) targets and determined the wave length of the characteristic X-rays that emanated from the target. He further showed that square root of the frequency of the shortest wave length (highest frequency) radiations of the X-rays from metal targets when plotted against the atomic weight of the respective metal provided a straight line *but a few elements were off the line*. A fine straight line plot was obtained when the square root of the frequencies of the characteristic X-rays were plotted against order numbers of the elements. This time there were no stray points. The order number has since been correlated with the atomic number of the elements.

The Periodic Table based on Moseley's atomic numbers did away with the irregularities that arise from the arrangement based on the atomic weight. For example, cobalt has an atomic weight of 58.9 atomic mass units (*amu*) and nickel has 58.7 *amu*. Hence according to Mendeleev's periodic law cobalt should be placed after nickel. Moseley's studies, on the contrary, adduced an atomic number 27 to cobalt and 28 to nickel and thus placed nickel after cobalt. Similar inversion of positions was eliminated for the pairs: argon, potassium; iodine, tellurium. The periodic law can now be restated as:

The properties of chemical elements and their compounds are periodic functions of the atomic numbers of the elements.

2.3. THE PERIODIC TABLE

All elements of very similar properties belong to a particular group. Elements of different properties are members of different groups. A period has to be traversed in order to arrive at an element of similar properties. The arrangement of some of the lighter elements is shown in Table 2.1. Only two elements, hydrogen and helium, form the first period. These two elements are followed by a period of eight elements. This period begins with the element lithium and ends in neon. The next period of eight elements begins with sodium and ends in argon. A glance

at Table 2.1 immediately reveals a periodicity in properties of the elements. Lithium, sodium and potassium form a close knit group. All these elements are

Table 2.1. The Lighter Elements of the Periodic Table

Group→ Period ↓	I	II	III	IV	V	VI	VII	0
First Period	H						(H)	He
Second Period	Li	Be	B	C	N	O	F	Ne
Third Period	Na	Mg	Al	Si	P	S	Cl	Ar
Fourth Period	K	Ca						

soft metals of low density and low melting point. All react with water to liberate hydrogen and produce metal hydroxides in solution. Their halides have the formula MX, have high melting points, and their oxides are of the type M_2O. They all form very similar hydrides MH. They form stable, crystalline bicarbonates, bisulphites, polyhalides etc. Chemical considerations place them together in the same group. Taking the group '0' we find again a close similarity in properties. Helium, neon and argon are remarkably inert during chemical reactions. They are monatomic. They form the family of noble gases. As we move along a period, say from sodium to magnesium, valence changes from one to two, magnesium forming $MgCl_2$, MgO etc. Boron, aluminium in group III are tervalent, forming BCl_3, $AlCl_3$ etc. and so on for the other groups. The first two members of the fourth period, potassium and calcium, rightly are members of group I and II respectively. After calcium there is a series of ten elements, scandium to zinc, which do not seem to fit properly into any of the eight groups. Mendeleev was conscious enough to recognise this problem. A solution was found out by arranging the elements in groups in order of atomic weights (later in order of atomic number) and allowing only one group position for iron, cobalt and nickel, a closely related triad (Tables 2.2 and 2.3). After this was done a superficial similarity emerged. For example, scandium in group III has really the group valence three and copper in group I has a valence + 1 at least in cuprous compounds. Mendeleev further divided the elements of a particular group into two subcolumns, which were termed subgroup A and subgroup B. All elements of a particular subgroup formed a coherent family, the chemistries being extremely close. Thus lithium, sodium, potassium, rubidium, caesium are all very closely related and belong to group IA. On the other hand, group IB comprises copper, silver and gold. Their properties compare favourably among them but vary from those of group IA. Both IB and IA have a formal similarity of monovalence in some of their compounds. The ten elements, from scandium to zinc, form a new group designated as the transition elements. Transition elements have already been defined (Chapter 1) as elements possessing partly filled d (or f) orbitals in elementary or ionic states. *Strictly speaking zinc should be left out of the transition group since both the element and its ion (only Zn^{2+} is known) have a filled d shell.* After zinc, there follow another eight elements whose properties are very

Table 2.2. Mendeleev's Table of 1871 (based on atomic weights)

Group I R_2O	Group II RO	Group III R_2O_3	Group IV RH_4 RO_2	Group V RH_3 R_2O_5	Group VI RH_2 RO_3	Group VII RH R_2O_7	Group VIII RO_4
H = 1							
Li = 7	Be = 9.4	B = 11	C = 12	N = 14	O = 16	F = 19	
Na = 23	Mg = 24	Al = 27.3	Si = 28	P = 31	S = 32	Cl = 35.5	
K = 39	Ca = 40	* = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Ni = 59. Co = 59
Cu = 63	Zn = 65	* = 68	* = 72	As = 75	Se = 78	Br = 80	
Rb = 85	Sr = 87	Y = 88	Zr = 90	Nb = 94	Mo = 96	* = 100	Ru = 104, Rh = 104, Pd = 106
Ag = 108	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	I = 127	
Cs = 133	Ba = 137	Di = 138	Ce = 140				
		Er = 178	La = 180	Ta = 182	W = 184		
Au = 199	Hg = 200	Tl = 204	Pb = 207	Bi = 208			Os = 195, Ir = 197. Pt = 198
			Th = 231		U = 240		

* indicates elements predicted

Table 2.3. Modern Version of Mendeleev's Periodic Table (based on atomic numbers)

Group Period	I A	I B	II A	II B	III A	III B	IV A	IV B	V A	V B	VI A	VI B	VII A	VII B	VIII	O
1	$_1$H															$_2$He
2	$_3$Li		$_4$Be		$_5$B		$_6$C		$_7$N		$_8$O		$_9$F			$_{10}$Ne
3	$_{11}$Na		$_{12}$Mg		$_{13}$Al		$_{14}$Si		$_{15}$P		$_{16}$S		$_{17}$Cl			$_{18}$Ar
4	$_{19}$K		$_{20}$Ca		$_{21}$Sc		$_{22}$Ti		$_{23}$V		$_{24}$Cr		$_{25}$Mn		$_{26}$Fe,$_{27}$Co,$_{28}$Ni	$_{36}$Kr
4		$_{29}$Cu		$_{30}$Zn		$_{31}$Ga		$_{32}$Ge		$_{33}$As		$_{34}$Se		$_{35}$Br		
5	$_{37}$Rb		$_{38}$Sr		$_{39}$Y		$_{40}$Zr		$_{41}$Nb		$_{42}$Mo		$_{43}$Tc		$_{44}$Ru,$_{45}$Rh,$_{46}$Pd	$_{54}$Xe
5		$_{47}$Ag		$_{49}$Cd		$_{49}$In		$_{50}$Sn		$_{51}$Sb		$_{52}$Te		$_{53}$I		
6	$_{55}$Cs		$_{56}$Ba		$_{37-71}$La*		$_{72}$Hf		$_{73}$Ta		$_{74}$W		$_{75}$Re		$_{76}$Os,$_{77}$Ir,$_{78}$Pt	$_{86}$Rn
6		$_{79}$Au		$_{80}$Hg		$_{81}$Tl		$_{82}$Pb		$_{83}$Bi		$_{84}$Po		$_{85}$At		
7	$_{87}$Fr		$_{88}$Ra		$_{89-104}$Ac**											

*Lanthanides $_{58}$Ce $_{59}$Pr $_{60}$Nd $_{61}$Pm $_{62}$Sm $_{63}$Eu $_{64}$Gd $_{65}$Tb $_{66}$Dy $_{67}$Ho $_{68}$Er $_{69}$Tm $_{70}$Yb $_{71}$Lu

**Actinides $_{90}$Th $_{91}$Pa $_{92}$U $_{93}$Np $_{94}$Pu $_{95}$Am $_{96}$Cm $_{97}$Bk $_{98}$Cf $_{99}$Es $_{100}$Fm $_{101}$Md $_{102}$No $_{103}$Lw

close to those of the second and third period. Gallium resembles group III elements, germanium resembles group IV and so on. This fourth period ends with the elements bromine and krypton. Bromine has properties close to those of chlorine and fluorine, and is rightly placed in group VII. Krypton, being a noble gas goes to group 0.

The fifth period begins with rubidium which has a chemistry typical of group IA. Then comes strontium with properties similar to those of calcium, and hence belongs to group IIA. Then follows another series of ten (strictly speaking nine) transition elements from yttrium to cadmium. After cadmium comes indium, an element close to gallium in properties and is therefore placed in group III. Tin, antimony, tellurium, iodine and xenon then go respectively to the groups IV, V, VI, VII and 0.

In the sixth period there is a total of thirty two elements. Following barium (II) there is a set of fifteen elements collectively called the rare earths or the lanthanides. They have an incomplete f shell, and since the f shell lies deeper down the outermost orbitals, these fifteen *elements form an inner transition series.* The lanthanides are then followed by another eight transition elements, and then by another nine regular or non-transition elements. Throughout the Periodic Table the following sets of transition elements occur, giving a total of 56 elements:

First series of transition elements: scandium (21) to copper (29)
Second series of transition elements: yttrium (39) to silver (47)
First series of inner transition elements: lanthanum (57) to lutecium (71)
Third series of transition elements: hafnium (72) to gold (79)
Second series of inner transition elements: actinium (89) to lawrencium (103).

In Mendeleev's 1871 Table (Table 2.2) there were only eight columns standing for the groups. He allowed one group for the triads (Fe, Co, Ni; Ru, Rh, Pd; Os, Ir, Pt) and allowed the subgroups to be represented within the same column (Tables 2.2, 2.3). He had left gaps for yet undiscovered element. He did not provide for the noble gases since none was discovered in his time. The elements of subgroup A and subgroup B of a particular group often varied widely in their chemical properties and yet they were placed in the same column in the 1871 Mendeleev Table (Table 2.2) and also in the modern version of the Mendeleev Table. For example, the alkalies and the currency metals possess hardly any chemical resemblance, yet these are all members of group I. In group VII the non-metallic halogens are widely different in their properties from the transition elements Mn, Tc and Re. These drawbacks have been removed in the currently used long form of the Periodic Table (Table 2.4), where the subgroups have been spread out on either side of group VIII. Instead of having eight columns as in the Mendeleev arrangement we now have a total of eighteen columns: fourteen of these are for seven subgroup A columns and seven subgroup B columns; each of the triads in group VIII has been assigned one column and the noble gases a new column. One major advantage of this arrangement is that we can at once have a clear picture about the position and chemical behaviour of elements. Thus strong electropositive

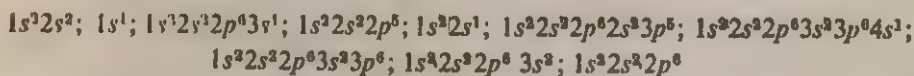Table 2.4. Long form Periodic Table of the Elements

Period	Gr. IA	Gr. IIA	Gr. IIIA	Gr. IVA	Gr. VA	Gr. VIA	Gr. VIIA	Group VIII			Gr. IB	Gr. IIB	Gr. IIIB	Gr. IVB	Gr. VB	Gr. VIB	Gr. VIIB	Gr. O
Period I	H 1																H 1	He 2
Period II	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
Period III	Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
Period IV	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Period V	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Period VI	Cs 55	Ba 56	La* 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Period VII	Fr 87	Ra 88	Ac** 89															

*Lanthanides	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
**Actinides	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lw 103

elements belonging to groups IA and IIA are placed at the left hand region of the Table, the electronegative elements belonging to groups IIIB, IVB, VB, VIB and VIIB occur at the right hand region of the Table and all transition elements at the central region of the Table (Table 2.4).

2.4. ELECTRONIC CONFIGURATION AND PERIODIC CLASSIFICATION

2.4.1. Classification of the Elements into Groups: Both atomic weights and atomic numbers have their origin in the nucleus, and both have been examined as a basis of the Periodic classification of elements. We have already seen that atomic number has an edge over atomic weight, being a more funda-mental yardstick of the periodicity of the properties of chemical elements. Atomic number again corresponds to the total number of electrons in an atom. Since extranuclear electrons are responsible for the chemical behaviour of elements it follows that on ultimate reckoning electronic configuration of elements must be connected with Periodic classification. Specifically the arrangement of the electrons in the outermost orbitals dictates the positions of the elements in the Periodic Table. This intimate connection is exposed by the following discussion.

We write below the electronic configurations of some randomly chosen elements:

$$1s^2 2s^2; \ 1s^1; \ 1s^2 2s^2 2p^6 3s^1; \ 1s^2 2s^2 2p^5; \ 1s^2 2s^1; \ 1s^2 2s^2 2p^6 2s^2 3p^5; \ 1s^2 2s^2 2p^6 3s^2 3p^0 4s^1;$$
$$1s^2 2s^2 2p^6 3s^2 3p^6; \ 1s^2 2s^2 2p^6 \ 3s^2; \ 1s^2 2s^2 2p^6$$

If the above electronic configurations are scrutinised from the view point of similarity in the outer orbital arrangement, the elements can be arranged in the following blocks:

$1s^1$	$1s^2 2s^2$	$1s^2 2s^2 2p^5$	$1s^2 2s^2 2p^6$
$1s^2 2s^1$	$1s^2 2s^2 2p^6 3s^2$	$1s^2 2s^2 2p^6 3s^2 3p^5$	$1s^2 2s^2 2p^6 3s^2 3p^6$
$1s^2 2s^2 2p^6 3s^1$			
$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$			
I	II	III	IV

In block I all the four elements have just one electron in an s orbital of the outermost quantum shell. This common feature generates similar chemical pro-perties, and because of their having one electron in the outermost quantum shell they are included in group I. The elements are hydrogen, lithium, sodium and potassium. Block II elements have two electrons in s shells of the outermost quantum shell, and are therefore members of group II. They are beryllium and magnesium. Block III has two elements with seven electrons in the outermost shell. Hence they are placed in group VII. *Periodic classification, therefore, is.*

based on the sorting out of the elements on the basis of the number of electrons in the outer quantum shell. The number of outermost quantum shell electrons is the group number to which the element belongs. With this yardstick the elements of block IV, having a common feature of a filled s and a filled p subshell, should be allotted to group VIII. Unfortunately group VIII had already been spared for the transition metal triads. Therefore the two elements in block IV, namely neon and argon, have been assigned a new group '0' which is symbolic of their extreme nobility. However as with many of our generalisations, exceptions also occur here —this relates to the arrangement of the transition elements. Our above generalisations hold very well for all regular or non-transition elements.

In the 'f' block inner transition elements with increasing atomic number electrons are added to the deep seated 'f' orbitals (Table 2.5). The nature of the higher quantum number energy levels of these elements is such that three electrons are removed comparatively easily to give the normal trivalent state. The ground state electronic configuration of the neutral lanthanide atoms is [Pd] $4f^n5s^25p^65d6s^2$ or [Pd] $4f^{n+1}5s^25p^66s^2$ reducing to [Pd] $4f^n5s^25p^6$ in the trivalent ions ($n = 0$ to 14 from La to Lu) (Table 2.5). As a consequence, the 'f' orbital electrons cannot participate in chemical reactions. These inner transition elements, from lanthanum to lutecium, are allotted just one group position in group III, following barium. Dominant tervalence justifies the inclusion of the lanthanides in Group III. The second inner transition series covers the actinides, the majority of which are man-made synthetic elements. Their electron distributions, broadly speaking, parallel those of the lanthanides, this time the deep seated $5f$ orbitals being progressively filled from actinium to lawrencium. Hence all these elements are given but one position in group III following radium.

In the d-block transition elements electrons are added successively to the penultimate shell, that is, to the d orbitals lying just below the highest quantum number s shells. The very small difference in energy between the d electrons ($3d$, $4d$ or $5d$) and the highest quantum number s ($4s$, $5s$ or $6s$ respectively) electrons (Fig. 1.18) makes these d electrons vulunerable to attack by chemical reagents, in addition to the outer orbital s electrons. Hence the chemistries of the d block transition elements are not similar to each other like the f block elements. Hence it will be unfair to restrict d block transition elements of a particular period to just one group position. They are, therefore, allotted successive groups. It is gratifying to note that the properties of a particular d block transition element are, to some extent at least, those expected of its position in a group. The long form of the Periodic Table has taken care of the problem of arrangement of these elements (Table 2.4) in particular.

It will be noted from Table 2.4 that hydrogen has been included in both group IA above the alkalies as also in group VIIB above the halogens. Like the alkalies it has one electron in an s shell and like the halogens it is just one electron short of the next noble gas (helium). In acids hydrogen loses the $1s$ electron and forms the cation, proton, which in water becomes H_3O^+. In alkali metal hydrides, hydrogen behaves as an anion (like the halides) with helium configuration.

Table 2.5. Electronic Configuration of Trivalent Lanthanide Ions

Lanthanide ion	Atomic Number	Core	4f	4f	4f	4f	4f	4f	4f	5s	5p	5p	5p
La³⁺	57	(Pd)	—	—	—	—	—	—	—	↑↓	↑↓	↑↓	↑↓
Ce³⁺	58	(Pd)	↑	—	—	—	—	—	—	↑↓	↑↓	↑↓	↑↓
Pr³⁺	59	(Pd)	↑	↑	—	—	—	—	—	↑↓	↑↓	↑↓	↑↓
Nd³⁺	60	(Pd)	↑	↑	↑	—	—	—	—	↑↓	↑↓	↑↓	↑↓
Pm³⁺	61	(Pd)	↑	↑	↑	↑	—	—	—	↑↓	↑↓	↑↓	↑↓
Sm³⁺	62	(Pd)	↑	↑	↑	↑	↑	—	—	↑↓	↑↓	↑↓	↑↓
Eu³⁺	63	(Pd)	↑	↑	↑	↑	↑	↑	—	↑↓	↑↓	↑↓	↑↓
Gd³⁺	64	(Pd)	↑	↑	↑	↑	↑	↑	↑	↑↓	↑↓	↑↓	↑↓
Tb³⁺	65	(Pd)	↑↓	↑	↑	↑	↑	↑	↑	↑↓	↑↓	↑↓	↑↓
Dy³⁺	66	(Pd)	↑↓	↑↓	↑	↑	↑	↑	↑	↑↓	↑↓	↑↓	↑↓
Ho³⁺	67	(Pd)	↑↓	↑↓	↑↓	↑	↑	↑	↑	↑↓	↑↓	↑↓	↑↓
Er³⁺	68	(Pd)	↑↓	↑↓	↑↓	↑↓	↑	↑	↑	↑↓	↑↓	↑↓	↑↓
Tm³⁺	69	(Pd)	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↑↓	↑↓	↑↓	↑↓
Yb³⁺	70	(Pd)	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑↓	↑↓	↑↓	↑↓
Lu³⁺	71	(Pd)	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

Table 2.6. Electronic Configurations of the Elements

Element/Symbol	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	5g	6s	6p	6d	6f	6g	6h	7s
1. Hydrogen (H)	1																					
2. Helium (He)	2																					
3. Lithium (Li)	2	1																				
4. Beryllium (Be)	2	2																				
5. Boron (B)	2	2	1																			
6. Carbon (C)	2	2	2																			
7. Nitrogen (N)	2	2	3																			
8. Oxygen (O)	2	2	4																			
9. Fluorine (F)	2	2	5																			
10. Neon (Ne)	2	2	6																			
11. Sodium (Na)	2	2	6	1																		
12. Magnesium (Mg)	2	2	6	2																		
13. Aluminium (Al)	2	2	6	2	1																	
14. Silicon (Si)	2	2	6	2	2																	
15. Phosphorus (P)	2	2	6	2	3																	
16. Sulphur (S)	2	2	6	2	4																	
17. Chlorine (Cl)	2	2	6	2	5																	
18. Argon (Ar)	2	2	6	2	6																	
19. Potassium (K)	2	2	6	2	6	—	1															
20. Calcium (Ca)	2	2	6	2	6	—	2															
21. Scandium (Sc)	2	2	6	2	6	1	2															
22. Titanium (Ti)	2	2	6	2	6	2	2															
23. Vanadium (V)	2	2	6	2	6	3	2															
24. Chromium (Cr)	2	2	6	2	6	5	1															
25. Manganese (Mn)	2	2	6	2	6	5	2															
26. Iron (Fe)	2	2	6	2	6	6	2															

Table 2.6. (Continued)

Element/Symbol	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	5g	6s	6p	6d	6f	6g	6h	7s
27. Cobalt (Co)	2	2	6	2	6	7	2															
28. Nickel (Ni)	2	2	6	2	6	8	2															
29. Copper (Cu)	2	2	6	2	6	10	1															
30. Zinc (Zn)	2	2	6	2	6	10	2															
31. Gallium (Ga)	2	2	6	2	6	10	2	1														
32. Germanium (Ge)	2	2	6	2	6	10	2	2														
33. Arsenic (As)	2	2	6	2	6	10	2	3														
34. Selenium (Se)	2	2	6	2	6	10	2	4														
35. Bromine (Br)	2	2	6	2	6	10	2	5														
36. Krypton (Kr)	2	2	6	2	6	10	2	6														
37. Rubidium (Rb)	2	2	6	2	6	10	2	6	—	—	1											
38. Strontium (Sr)	2	2	6	2	6	10	2	6	—	—	2											
39. Yttrium (Y)	2	2	6	2	6	10	2	6	1	—	2											
40. Zirconium (Zr)	2	2	6	2	6	10	2	6	2	—	2											
41. Niobium (Nb)	2	2	6	2	6	10	2	6	4	—	1											
42. Molybdenum (Mo)	2	2	6	2	6	10	2	6	5	—	1											
43. Technetium (Tc)	2	2	6	2	6	10	2	6	6	—	1											
44. Ruthenium (Ru)	2	2	6	2	6	10	2	6	7	—	1											
45. Rhodium (Rh)	2	2	6	2	6	10	2	6	8	—	1											
46. Palladium (Pd)	2	2	6	2	6	10	2	6	10	—	—											
47. Silver (Ag)	2	2	6	2	6	10	2	6	10	—	1											
48. Cadmium (Cd)	2	2	6	2	6	10	2	6	10	—	2											
49. Indium (In)	2	2	6	2	6	10	2	6	10	—	2	1										
50. Tin (Sn)	2	2	6	2	6	10	2	6	10	—	2	2										
51. Antimony (Sb)	2	2	6	2	6	10	2	6	10	—	2	3										
52. Tellurium (Te)	2	2	6	2	6	10	2	6	10	—	2	4										

Table 2.6. (Continued)

Element/Symbol	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	5g	6s	6p	6d	6f	6g	6h	7s
53. Iodine (I)	2	2	6	2	6	10	2	6	10	—	2	5	—	—	—							
54. Xenon (Xe)	2	2	6	2	6	10	2	6	10	—	2	6	—	—	—							
55. Caesium (Cs)	2	2	6	2	6	10	2	6	10	—	2	6	—	—	—	1						
56. Barium (Ba)	2	2	6	2	6	10	2	6	10	—	2	6	—	—	—	2						
57. Lanthanum (La)	2	2	6	2	6	10	2	6	10	—	2	6	1	—	—	2						
58. Cerium (Ce)	2	2	6	2	6	10	2	6	10	2	2	6	—	—	—	2						
59. Praseodymium (Pr)	2	2	6	2	6	10	2	6	10	3	2	6	—	—	—	2						
60. Neodymium (Nd)	2	2	6	2	6	10	2	6	10	4	2	6	—	—	—	2						
61. Promethium (Pm)	2	2	6	2	6	10	2	6	10	5	2	6	—	—	—	2						
62. Samarium (Sm)	2	2	6	2	6	10	2	6	10	6	2	6	—	—	—	2						
63. Europium (Eu)	2	2	6	2	6	10	2	6	10	7	2	6	—	—	—	2						
64. Gadolinium (Gd)	2	2	6	2	6	10	2	6	10	7	2	6	1	—	—	2						
65. Terbium (Tb)	2	2	6	2	6	10	2	6	10	9	2	6	—	—	—	2						
66. Dysprosium (Dy)	2	2	6	2	6	10	2	6	10	10	2	6	—	—	—	2						
67. Holmium (Ho)	2	2	6	2	6	10	2	6	10	11	2	6	—	—	—	2						
68. Erbium (Er)	2	2	6	2	6	10	2	6	10	12	2	6	—	—	—	2						
69. Thulium (Tm)	2	2	6	2	6	10	2	6	10	13	2	6	—	—	—	2						
70. Ytterbium (Yb)	2	2	6	2	6	10	2	6	10	14	2	6	—	—	—	2						
71. Lutecium (Lu)	2	2	6	2	6	10	2	6	10	14	2	6	1	—	—	2						
72. Hafnium (Hf)	2	2	6	2	6	10	2	6	10	14	2	6	2	—	—	2						
73. Tantalum (Ta)	2	2	6	2	6	10	2	6	10	14	2	6	3	—	—	2						
74. Tungsten (W)	2	2	6	2	6	10	2	6	10	14	2	6	4	—	—	2						
75. Rhenium (Re)	2	2	6	2	6	10	2	6	10	14	2	6	5	—	—	2						
76. Osmium (Os)	2	2	6	2	6	10	2	6	10	14	2	6	6	—	—	2						
77. Iridium (Ir)	2	2	6	2	6	10	2	6	10	14	2	6	7	—	—	2						
78. Platinum (Pt)	2	2	6	2	6	10	2	6	10	14	2	6	9	—	—	1						

Table 2.6. (Continued)

Element/Symbol	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	5g	6s	6p	6d	6f	6g	6h	7s
79. Gold (Au)	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	1	—	—	—	—	—	
80. Mercury (Hg)	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2	—	—	—	—	—	
81. Thallium (Tl)	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2	1	—	—	—	—	
82. Lead (Pb)	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2	2	—	—	—	—	
83. Bismuth (Bi)	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2	3	—	—	—	—	
84. Polonium (Po)	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2	4	—	—	—	—	
85. Astatine (At)	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2	5	—	—	—	—	
86. Radon (Rn)	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2	6	—	—	—	—	
87. Francium (Fr)	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2	6	—	—	—	—	1
88. Radium (Ra)	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2	6	—	—	—	—	2
89. Actinium (Ac)	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2	6	1	—	—	—	2
90. Thorium (Th)	2	2	6	2	6	10	2	6	10	14	2	6	10	—	—	2	6	2	—	—	—	2
91. Protactinium (Pa)	2	2	6	2	6	10	2	6	10	14	2	6	10	2	—	2	6	1	—	—	—	2
92. Uranium (U)	2	2	6	2	6	10	2	6	10	14	2	6	10	3	—	2	6	1	—	—	—	2
93. Neptunium (Np)	2	2	6	2	6	10	2	6	10	14	2	6	10	4	—	2	6	1	—	—	—	2
94. Plutonium (Pu)	2	2	6	2	6	10	2	6	10	14	2	6	10	6	—	2	6	—	—	—	—	2
95. Americium (Am)	2	2	6	2	6	10	2	6	10	14	2	6	10	7	—	2	6	—	—	—	—	2
96. Curium (Cm)	2	2	6	2	6	10	2	6	10	14	2	6	10	7	—	2	6	1	—	—	—	2
97. Berkelium (Bk)	2	2	6	2	6	10	2	6	10	14	2	6	10	8	—	2	6	1	—	—	—	2
98. Californium (Cf)	2	2	6	2	6	10	2	6	10	14	2	6	10	10	—	2	6	—	—	—	—	2
99. Einsteinium (Es)	2	2	6	2	6	10	2	6	10	14	2	6	10	11	—	2	6	—	—	—	—	2
100. Fermium (Fm)	2	2	6	2	6	10	2	6	10	14	2	6	10	12	—	2	6	—	—	—	—	2
101. Mendeleevium (Md)	2	2	6	2	6	10	2	6	10	14	2	6	10	13	—	2	6	—	—	—	—	2
102. Nobelium (No)	2	2	6	2	6	10	2	6	10	14	2	6	10	14	—	2	6	—	—	—	—	2
103. Lawrencium (Lw)	2	2	6	2	6	10	2	6	10	14	2	6	10	14	—	2	6	1	—	—	—	2

The electronic configurations of all the elements so far known are included in Table 2.6. The electron population of different orbitals has been indicated by appropriate numbers, instead of arrows. The electronic configurations of the actinides are not known with as much certainty as for other elements. However those given in the Table are the generally accepted ones.

2.4.2. Capacities of Periods: It is interesting to note that there is some connection between the electronic configuration of the elements and the accommodation capacities of the periods. Note that the 1s orbital can have only two electrons. Hence only two elements (H and He) complete Period I (Table 2.4). Next the $n = 2$ shell starts. It has a maximum capacity of $2n^2$ i.e., 8 electrons. In keeping with this we find that Period II has eight elements (lithium to neon). Then we have the filling of the 3s and 3p orbitals with a total capacity of eight elements. This shell has 3d orbitals but because of the lower energy of the 4s orbital than the 3d orbitals (Fig. 1.19), the 3d level is not immediately filled. Thus Period III again shows eight elements from sodium ($1s^2 2s^2 2p^6 3s^1$) to argon ($1s^2 2s^2 2p^6 3s^2 3p^6$). The next Period IV shows gradual filling of the 4s, 3d and 4p orbitals giving a total of $2 + 10 + 6 = 18$ elements from potassium to krypton. Period V registers the filling of 5s, 4d and 5p orbitals i.e., a total of 18 elements from rubidium to xenon. The next Period VI includes 6s, 4f, 5d and 6p—a total of 32 elements from caesium to radon. Periodicity and capacities of periods are closely connected with gradual filling up of the orbitals by electrons. *The beauty of Mendeleev's discovery lies in the fact that in no Period does the number of elements exceed that admitted by the electron accommodation capacity of a particular quantum shell or subshell.*

STUDY QUESTIONS

1. How would you proceed to assign positions to elements of atomic numbers 4, 5, 11, 17 in the Periodic Table?

2. Hydrogen with a single electron can also be placed in group VII. Will it be inconsistent with its properties?

3. If the lanthanides could be accommodated as a family in one position in the Periodic Table why can't we do it for the elements of the first transition series?

4. There is a connection between the capacities of the periods and the electronic configurations. Discuss.

5. In what regions of the Periodic Table are to be expected elements with smallest values of ionisation potential and largest values of electron affinity? (Wait till Chapter 4).

6. Try to predict on the basis of electronic configuration and relative ordering of the energy levels, the properties of regular or non-transition elements and transition elements.

7. Where are the following types of elements found in the Periodic Table? (a) metals (b) non-metals (c) most electropositive elements (d) most electronegative elements.

8. From the position of the elements in the Periodic Table predict the formulas for the compounds formed between (a) Si and H (b) Si and F (c) Al and O (d) S and Cl (e) Na and H (f) Ne and F

9. From lithium to neon there are eight elements. Show from an appreciation of electron distribution that there can be no less or no more than eight elements in this Period.

10. In which groups of the Periodic Table will you include the elements with electronic configurations:

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ ;\ 1s^2\ 2s^2\ ;\ 1s^2\ 2s^2\ 2p^6\ \text{and}\ 1s^2\ 2s^2\ 2p^6.$$

11. Mention the anomalies in Mendeleev's Periodic Table. How were these anomalies taken care of?

12. In what respects the Periodic Table is useful to the chemists?

13. State the electronic configurations of the noble gases and discuss their position in the Periodic Table.

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Atomic Weights

Atomic weights formed the basis of the Periodic classification suggested by Mendeleev. The basis had since been changed to atomic numbers, as these latter were found to be more fundamental to the understanding of chemical properties. The atomic weights, however, have not lost their significance or usefulness. The atomic weights are still the very basis of all quantitative chemical analyses calculation of energy, mass defects, etc. etc., and are therefore of paramount importance in all our chemical and physical pursuits. Since Dalton's time our ideas of the atomic weights had undergone refinements, and it is the purpose of this Chapter to outline these refinements.

3.1. THE ATOMIC WEIGHTS AND RELATED TERMS

As our knowledge of the chemical world continued to grow a question that confronted chemists was what is the relative weights of the atoms of different elements and how to express these relative weights. It was but natural to ask how much an atom of sodium or an atom of chlorine weighed. The answer to such questions was given in the form of relative weights of the atoms, expressed in terms of their atomic weights:

The atomic weight of an element is a number that says how much heavy an atom of a particular element is compared to an atom of another element taken as a reference.

The atomic weights were regarded, prior to our recognising isotopes, as invariant constants of nature. It was thought that the precision attainable in the determination of atomic weights was limited only by experimental techniques. The confidence in the invariance of atomic weights has now been totally shaken as a result of the discovery of isotopic species of many elements. Atomic weights will therefore remain constant only for those elements that have no naturally occurring isotopes. The following observations are relevant in this connection:

1. The term atomic weight, when used without any qualification, refers to the atomic weight of an element, as it occurs in nature. Atomic weight and atomic mass are often used synonymously.

2. A naturally occurring isotopic element occurs in different isotopic species, and hence atomic weight of such an element is but a weighted average of the atomic weights of the different isotopic species taking into consideration their relative abundances.

3. The mass of an atom is a definite quantity and is generally expressed in atomic mass unit, the definition of which will be given a little later. However the accuracy with which the absolute masses of atoms can be experimentally determined is more limited than the relative masses, that is, the ratio of the mass of an element to that of some other atomic particle. Actual measurements are made on a relative, rather than on an absolute basis. 'Atomic weights' are really 'atomic weight ratios'. Atomic weights are thus dimensionless numbers.

4. Nuclear masses are due to the nucleons (protons and neutrons). For isotopic species the nuclear masses are different whereas for an anisotopic species the nuclear mass is fixed. Atomic mass of an element minus the mass of the electrons forming the atom, will provide the nuclear mass.

5. Two scales, namely a chemical scale (based on natural oxygen given a weight 16) and a physical scale (based on óxygen-16 isotope given a weight 16) were in use for the purpose of expressing atomic weights. These two scales have now been discarded and a unified scale based on carbon-12 isotope has been accepted. The carbon-12 scale is also a physical scale and its acceptance has been prompted because the atomic weights derived from the chemical scale differed insignificantly from those based on carbon-12 scale.

3.2. THE CHEMICAL AND PHYSICAL SCALES OF ATOMIC WEIGHTS

Atomic weights are expressed in relation to a reference, the choice of the reference being dictated by the number of elements whose weight equivalence to the reference could be determined directly. It was also recognised very early that the choice of a reference weight to be assigned to the reference element had to be arbitrary. For example, it may sound amusing now that Berzelius who favoured oxygen as the reference element used, for some time at least, 100 as its weight. Several references have been proposed so far. Hydrogen was used very early as a reference since this was the lightest element known, and its atomic weight was assumed 1. The use of hydrogen was later found to be of limited merit since not many elements combined with hydrogen to produce pure, stoichiometric compounds. Search for another reference began and it was observed that oxygen formed more binary and other types of chemical compounds with a wider range of elements. From a study of the reactions of hydrogen and oxygen forming water in atomic ratio (2 hydrogen to 1 oxygen) and by weight (1 part of hydrogen to 8 parts of oxygen) oxygen was assigned an atomic weight 16. The two references $H = 1.000$ and $O = 16.000$ were supposed to be equivalent to each other for

fixing the atomic weights of other elements. In view of our current ideas of the structure of atoms, the assignment of unit weight to hydrogen and sixteen to oxygen must be considered as fortunate selections since 1 and 16 correspond to the mass numbers of these elements.

The scale of atomic weight with natural oxygen of relative weight 16 taken as the reference is called the chemical scale of atomic weights.

It can be guessed that the chemical scale based on natural oxygen ($O = 16.000$) will stay good so long as no one doubted the singularity of its atomic composition. Slowly but steadily physicists have started to devise more and more accurate methods for determining the masses of different elements. Aston developed his mass spectrograph where the mass of an element could be determined with a precision of 1 in 100,000. Natural oxygen was found to be a mixture of as many as three isotopes of mass numbers 16, 17 and 18 with percentage abundances of 99.575, 0.039 and 0.204 respectively. The true mass of natural oxygen is therefore:

$$(16 \times 0.99757) + (17 \times 0.00039) + (18 \times 0.00204) = 16.00447$$

Aston decided to use the exact number 16 as the relative mass of oxygen isotope-16 as a reference and thus introduced a new scale of atomic weights.

The scale of atomic weights with O-16 isotope of relative weight 16 taken as the reference is called the physical scale of atomic weights.

In chemical determinations of atomic weights natural oxygen, against which all weight equivalence reactions were studied, was assumed to have a value of 16.000, instead of the physically determined value of 16.00447. The chemical atomic weights include the heavier isotopes within $O = 16.000$. Therefore, the physical atomic weights are always larger than the chemical atomic weights by the ratio 16.00447 : 16.00000, that is:

Physical atomic weight of an element $= 1.00028 \times$ chemical atomic weight.

3.3. THE UNIFIED CARBON-12 SCALE OF ATOMIC WEIGHTS

The existence of two atomic weight scales was causing concern to chemists and physicists. A case for adoption of a unified scale for atomic weights therefore arose. Scrapping of the chemical scale altogether by the physical scale meant upward revision of all precisely determined chemical data by a factor of 0.028% and to extend the correction to all standard physicochemical data on the chemical scale. This situation was clearly not acceptable to chemists. On the other hand physicists demanded that atomic weights must be expressed taking the mass of an isotopic species as a reference. A compromise was found out that honoured the claims of both the physicists and the chemists. Mass spectrographic analysis of natural carbon showed 98.89% abundance of carbon-12 and 1.11% abundance of carbon-13 isotope. The percent abundance of carbon-14 in nature was negligible for the purpose. This gave a mass of 12.01115 to the isotopic mixture on granting a mass of 12 to carbon-12 and of mass 13 to carbon-13 isotope. The chemically determined atomic weight of carbon, however, was found to be 12.011617. The physical scale (O-16) value was 12.014921. Consideration of several other atomic

weights expressed on the chemical scale and on the carbon-12 scale led to the conclusion that the chemical scale atomic weights need to be reduced by only 0.004% for conversion to the carbon-12 scale atomic weights. A comparison of some atomic weights on the three scales is given in Table 3.1. This made chemists happy because their painstaking determination of atomic weights still stood the

Table 3.1. Comparison of the Chemical Scale, the Physical Scale and the Unified Carbon-12 Mass Scale

Species	Chemical scale	Physical Scale (O-16) = 1.00028 × Chemical Scale	Unified Carbon-12 Scale = 0.99967 × Chemical Scale
H (natural)	1.008011	1.008288	1.007967
C (natural)	12.01.617	12.014921	12.011150
O (natural)	16.00000	16.00447	15.999312
H-1	1.007865	1.008142	1.007822
O-16	15.995691	16.00000	15.994912
C-12	12.000516	12.003816	12.00000

ground, and the correction figure being small any recalculation and reevaluation of standard physi-chemical data were hardly necessary. The acceptance of the carbon-12 scale also made the physicists happy because their dien and of using a single isotope as the reference was recognised. So the current position is that all atomic weights are expressed in the unified carbon-12 scale. It is important to mention that any change in atomic weight scale would affect gravimetric factors, since all atomic weights would be changed in equal proportions.

3.4. SOME DEFINITIONS

Based on the unified scale the following definitions are to be noted:

A. The atomic weight of an element is a number that says how much heavy an atom of an element is compared to one-twelfth of an atom of carbon-12 isotope.

B. The gram atomic weight of an element is the weight in grams that contains the same number of atoms as twelve grams of carbon-12 isotope. It should be noted that while the atomic weight of an element is dimensionless, its gram atomic weight has the unit of grams. It is often loosely stated that the gram atomic weight is the atomic weight expressed in grams.

C. Atomic mass unit (amu) is exactly the one-twelfth of the mass of a carbon-12 atom. The mass of an atom expressed in amu is numerically equal to its atomic weight on the carbon-12 scale. Since 6.023×10^{23} (Avogadro number) atoms of carbon-12 weigh 12 gm each carbon-12 atom weighs $(12/6.023) \times 10^{-23}$ gm. Therefore,

$$1 \ amu = \frac{12}{6.023} \times \frac{1}{12} \times 10^{-23} g = 1.6603 \times 10^{-24} g$$

D. The molecular weight of a compound is a number that indicates how heavy a molecule of the compound is compared to one-twelfth of an atom of carbon-12 isotope.

· E. The gram molecular weight of a compound is the weight in grams that contains the same number of molecules as the number of atoms present in twelve grams of carbon-12 isotope. Loosely it is the molecular weight expressed in grams.

3.5. DETERMINATION OF ATOMIC WEIGHTS

3.5.1. Chemical Stoichiometry. The essence of the classical methods of determining atomic weights was to effect carefully a set of quantitative chemical conversions on a chosen substance, and then to determine very precisely the ratio of the combining weight of the element (whose atomic weight was being sought) and that of a reference element. Preferably only the desired element and the reference element were involved in the observed reaction. If other elements were participants in these conversions, their atomic weights had to be determined by other independent measurements. The essential data are the combining weights and a knowledge of the valences of the elements involved in the chemical conversions.

The principles involved in the chemical determinations are simple enough but obtaining precise data involves considerable experimental problems. Apart from the necessity of very accurate weighing, the technique involves quantitative conversion of one substance to another. The purity of the materials at all stages must be of the highest order and the compounds must conform to some exact stoichiometry. The experimental problems relate to meticulous drying of the materials, their handling in suitable atmosphere and precision weighing. Fortunately a group of brilliant experimentalists emerged during the first decade of this century, who overcame all the difficult problems and reported atomic weights much more accurrately than those obtained by earlier workers. The 1914 award of Nobel Prize for chemistry went to Richards for his works on atomic weights. The award is remarkable because it was given for refinements of existing knowledge rather than for original discovery.

Some atomic weight determinations are now discussed.

Stas's works. In order to determine the atomic weight of silver precisely Stas made use of the reaction between silver and chlorine. A known weight of pure silver was heated in a stream of dry and pure chlorine gas in a glass tube and the resulting silver chloride was weighed. He also dissolved a known quantity of silver in pure nitric acid and precipitated the silver as silver chloride and weighed. 35.45 gm of chlorine combined with 107.94 gm of silver to give 143.39 gm of AgCl. Taking the atomic weight of chlorine as 35.45. the atomic weight of silver was found out to be 107.94.

For determination of atomic weight of nitrogen Stas converted a weighed amount of KCl to KNO_3 by repeated treatment with nitric acid. The ratio of KCl : KNO_3 = 74.59 : 101.175 was obtained. Putting in the values of K(= 39.14) and O(= 16.00) we have:

$$\frac{74.59}{39.14 - N + 48} = \frac{74.59}{101.175} \text{ whence } N = 14.035$$

Alternatively a weighed amount of silver was dissolved in HNO_3, the solution dried and the silver nitrate fused and dried. Stas calculated the ratio Ag: $AgNO_3$ = 100 : 157.484. Then

$$\frac{107.94}{107.94 + N + 48} = \frac{100}{157.484} \text{ whence } N = 14.05$$

Richards Works. Richards introduced many improvements in the experimental techniques including purification of materials, careful drying, weighing in quartz vessels, and working in suitable atmosphere (of hydrogen etc). Stas's works suffered from some sources of error, such as solubility of silver chloride, occulsion of oxygen by silver, inadequate washing due to a large quantity of material etc.

Richards developed a special bottling apparatus (Fig. 3.1). The apparatus consists of a quartz tube A fitted by a ground glass joint to another glass tube B with a pocket C. A platinum boat D containing the substance was put inside the quartz tube. The weighing bottle E was put into B and its stopper S into the pocket.
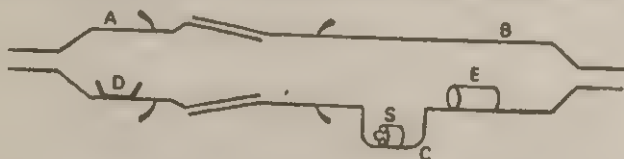
FIG. 3.1. Richards' bottling apparatus

The boat was heated in a current of some dry gas. It was then cooled, the gas in the bottling apparatus replaced by dry air and the boat pushed by a rod through A into the weighing bottle. The tube B was then rotated until the stopper S faced the bottle. The stopper was then pushed into the mouth of the bottle. The stoppered bottle was then removed and weighed.

In order to avoid the uncertainties in the usual gravimetric estimation of silver as silver chloride, Richards used a nephelometric method for the purpose. The amount of silver chloride that was suspected to have remained in solution after precipitation as AgCl was determined by the addition of excess silver nitrate whereby due to common ion effect some small amount of silver chloride came out of solution showing opalescence. This opalescence was compared with a standard in a nephelometer by passing bright light through the solution. However the nephelometric method has been criticised by chemists.

With these modifications Richards and his students proceeded to obtain accurate atomic weight data for silver, nitrogen and chlorine. Three sets of reactions were quantitatively studied for the purpose:

(1) determination of the amount of AgCl from a known amount of Ag
(2) determination of the amount of AgCl from a known amount of NH_4Cl
(3) determination of the amount of $AgNO_3$ from a known amount of Ag

(1) Silver nitrate was recrystallised fifteen times. This was then reduced to pure silver and weighed. This silver was then treated with very pure nitric acid (which was previously distilled repeatedly) and the silver precipitated by very

pure sodium chloride. The silver chloride was determined by gravimetric and nephelometric procedures; result: 1.00000 gm of silver gave 1.32867 gm AgCl.

(2) Pure ammonium chloride was obtained at considerable pains. Ammonium sulphate was treated with $KMnO_4$ to destroy any organic impurity. This was then treated with pure lime and the ammonia was absorbed in HCl. The crude NH_4Cl obtained from the solution was sublimed to give the pure salt. A weighed amount was treated with very pure silver nitrate and the silver chloride determined as above.

result: 0.373217 gm of NH_4Cl gave 1.00000 gm AgCl.

(3) Very pure silver, as obtained above, was dissolved in pure HNO_3 and the solution evaporated to dryness in dry air.

result: 1.00000 gm of silver gave 1.57497 gm of $AgNO_3$

Now let $\qquad \dfrac{AgCl}{Ag} = a; \dfrac{NH_4Cl}{AgCl} = b; \dfrac{AgNO_3}{Ag} = c$

If the atomic weights of Ag, Cl and N be assumed x, y and z respectively, and if atomic weights of H and O are taken as 1.0076 and 16.000 respectively we have:

$$x + y = ax \qquad \qquad \ldots (1)$$
$$y + z + 4.0304 = b(x + y) \qquad \ldots (2)$$
$$x + z + 48.000 = cx \qquad \qquad \ldots (3)$$

Putting the value of z from (3) into (2) we have:

$$(c-1)x - bx + (1-b)y = 43.9696$$

But according to equation (1), $y = (a-1)x$ so that

$$x = \frac{43.9696}{c-1-b+(1-b)(a-1)} = \frac{43.9696}{c-2+a-ab}$$

Since a, b and c are all known from experiments, atomic weight of silver turns out to be 107.88. Similarly the other two were worked out: N = 14.008 and Cl = 35.457.

Honigschmid's works. Honigschmid and coworkers arrived at the atomic weight of silver from another set of chemical conversions. A weighed amount of $Ba(ClO_4)_2$ was dried in a furnace at 260°C in a current of pure and dry air. The sample was then manipulated by specially devised techniques into a vacuum weighing bottle and its weight recorded. It was then returned to the furnace and heated in a stream of dry HCl gas at 200°C and finally at 550°C so as to convert the Ba $(ClO_4)_2$ to $BaCl_2$. This was weighed again in vacuo. Weighing in vacuo was done with a view to minimising occlusion of oxygen by $BaCl_2$. The chloride in $BaCl_2$ was finally estimated with silver ion by nephelometric method. Thus precise data were collected on the weights of $Ba(ClO_4)_2$, $BaCl_2$ and AgCl corresponding to $BaCl_2$. It can be seen that the loss of weight in going from Ba $(ClO_4)_2$ to $BaCl_2$ gives the ratio of 8O: $BaCl_2$. Then since $BaCl_2$ was converted quantitatively to silver chloride the ratio of 8O : 2AgCl is available. Further since we know from other workers' experiments how much silver combines with how much chlorine it is possible to deduce the ultimate ratio of 8O : 2Ag whence on the assumption of O = 16.000 the atomic weight of silver was calculated as 107.88.

3.5.2. Mass Spectrography. Mass spectrograph is basically an equipment that allows determination of the charge to mass ratio of positive ions. This determination of mass is achieved by an examination of the positive ions in electric and magnetic fields.

Positive ions are produced in an ionisation chamber either by heating salts of the metallic element which is being examined or by bombarding a suitable volatile compound with a stream of electrons emitted from a heated filament. Arrangement inside the ionisation chamber is such that electrons or negative ions that might be produced are collected on the positive plate serving as a trap for electrons or negative ions. Only the positive ions emerge from the ionisation chamber and a narrow beam is selected out by suitable slits. This beam is next accelerated by passage through an electric field PP ($\sim$ 2000 volts) when the positive ions of different charge to mass ratios spread out.
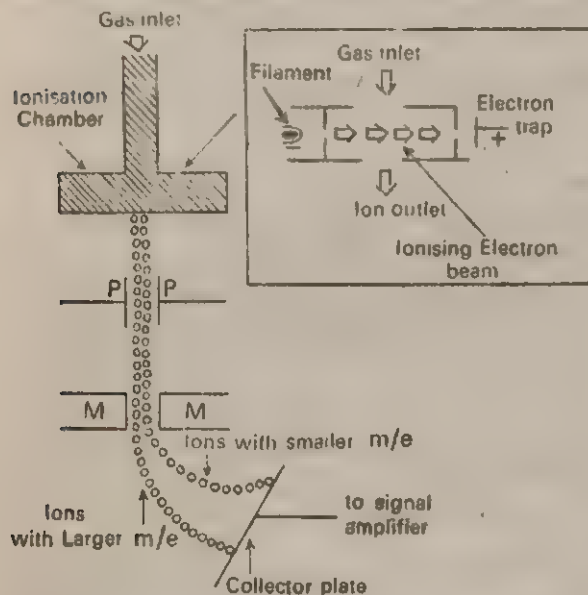
FIG. 3.2. Schematic diagram of mass spectrograph

These are then passed through a magnetic field MM applied at 90° to the electric field. By this technique the different positive ions are deflected to different degrees and are recorded on a photographic plate or brought on to a collector plate with amplifier device (Fig. 3.2) The source and the path through which the ions pass must be kept under a vacuum to provide a long mean free path for the ions.

For a given accelerating voltage and magnetic field strength, the extent to which the ion beam is deflected depends upon the charge and mass of the ions. The deflection of an ion is inversely related to its mass but directly related to its charge. The energy of the ions in an electric field is Xe (X = strength of the electric field and e = charge on the positive ion). This energy is kinetic energy since the electric field accelerates the positive ions. Then,

$$Xe = \tfrac{1}{2}mv^2 (v = \text{velocity of the positive ion})$$

In the magnetic field the centrifugal force mv^2/r (r = radius of curvature) is balanced by the centripetal force Hev (H = strength of the magnetic field). Then,

$$Hev = \frac{mv^2}{r} \qquad \therefore He = \frac{mv}{r} \text{ and } v^2 = \frac{H^2e^2r^2}{m^2}$$

$$Xe = \tfrac{1}{2}mv^2 = \frac{mH^2e^2r^2}{2m^2}; \quad X = \frac{H^2r^2}{2} \cdot \frac{e}{m}$$

Finally $$\frac{e}{m} = \frac{2X}{H^2r^2}$$

From practical standpoint accurate determination of H and r is difficult. and is avoided in the determination of atomic weights. A known positive ion. say $+1$ ion of carbon-12 is used as a reference. Using a known accelerating voltage and a certain magnetic field H, the position of the monopositive carbon-12 ions on the collector plate (or the photographic plate) is noted. Then mono positive ions of the element, say A, whose mass is to be determined is brought to the same point on the collector plate by adjusting the accelerating voltage only (leaving the magnetic field unchanged). Under such situation the two positive ions have the same charge, are under the same magnetic field H and have the same radius of curvature r. The two ions having the same 'e' but different mass we have:

$$\frac{e}{m} = \frac{2X}{H^2r^2} \; ; \; \frac{e}{m'} = \frac{2X'}{H^2r^2} \cdot$$

$$\therefore \quad \frac{e}{m} \Big/ \frac{e}{m'} = \frac{2X}{H^2r^2} \Big/ \frac{2X'}{H^2r^2} \; ; \; \frac{m'}{m} = \frac{X}{X'}$$

Thus $$\frac{\text{mass of carbon-12}}{\text{mass of A}} = \frac{\text{voltage for A}}{\text{voltage for carbon-12}}$$

The two voltages, and the mass of carbon-12 being known, we can calculate the mass (atomic weight) of A.

3.6. TABLE OF ATOMIC WEIGHTS

Below we give the atomic weights of elements on the unified carbon-12 scale. The numbers in parentheses denote the mass number of the longest lived or best known isotope.

Table 3.2. Table of Atomic Weights (based on carbon-12 = 12.000)

Element	Symbol.	Atomic Number	Atomic Weight
Actinium	Ac	89	227
Aluminium	Al	13	26.98
Americium	Am	95	(243)
Antimony	Sb	51	121.75
Argon	Ar	18	39.948
Arsenic	As	33	74.92
Astatine	At	85	(210)
Barium	Ba	56	137.34
Berkelium	Bk	97	(249)
Beryllium	Be	4	9.012
Bismuth	Bi	83	208.98
Boron	B	5	10.81
Bromine	Br	35	79.909

Table 3.2. (Continued)

Element	Symbol	Atomic Number	Atomic Weight
Cadmium	Cd	48	112.40
Calcium	Ca	20	40.08
Californium	Cf	98	(251)
Carbon	C	6	12.01115
Cerium	Ce	58	140.12
Caesium	Cs	55	132.91
Chlorine	Cl	17	35.453
Chromium	Cr	24	52.00
Cobalt	Co	27	58.933
Copper	Cu	29	63.54
Curium	Cm	96	(247)
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	(254)
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	(253)
Fluorine	F	9	19.00
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.59
Gold	Au	79	196.97
Hafnium	Hf	72	178.49
Helium	He	2	4.003
Holmium	Ho	67	164.93
Hydrogen	H	1	1.007967
Indium	In	49	114.82
Iodine	I	53	126.90
Iridium	Ir	77	192.20
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lawrencium	Lw	103	(257)
Lead	Pb	82	207.19
Lithium	Li	3	6.939
Lutecium	Lu	71	174.97
Magnesium	Mg	12	24.312
Manganese	Mn	25	54.94
Mendeleevium	Md	101	(256)
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24

Table 3.2. (Continued)

Element	Symbol	Atomic Number	Atomic Weight
Neon	Ne	10	20.183
Neptunium	Np	93	(237)
Nickel	Ni	28	58.71
Niobium	Nb	41	92.91
Nitrogen	N	7	14.007
Nobelium	No	102	(253)
Osmium	Os	76	190.2
Oxygen	O	8	15.99943
Palladium	Pd	46	106.4
Phosphorus	P	15	30.974
Platinum	Pt	78	195.09
Plutonium	Pu	94	(242)
Polonium	Po	84	210
Potassium	K	19	39.102
Praseodymium	Pr	59	140.907
Promethium	Pm	61	(147)
Protactinium	Pa	91	(231)
Radium	Ra	88	226.05
Radon	Rn	86	222
Rhenium	Re	75	186.23
Rhodium	Rh	45	102.905
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.07
Samarium	Sm	62	150.35
Scandium	Sc	21	44.956
Selenium	Se	34	78.96
Silicon	Si	14	28.086
Silver	Ag	47	107.87
Sodium	Na	11	22.9898
Strontium	Sr	38	87.62
Sulphur	S	16	32.064
Tantalum	Ta	73	180.948
Technetium	Tc	43	(99)
Tellurium	Te	52	127.60
Terbium	Tb	65	158.924
Thallium	Tl	81	204.37
Thorium	Th	90	232.038
Thulium	Tm	69	168.934
Tin	Sn	50	118.69
Titanium	Ti	22	47.90
Tungsten	W	74	183.85
Uranium	U	92	238.03

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Table 2.3. (Continued)

Element	Symbol	Atomic Number	Atomic Weight
Vanadium	V	23	50.942
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.905
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

STUDY QUESTIONS

1. The chloride of a metal contains 60.6 per cent chlorine by weight. If the combining ratio (by atom) is 1 : 1 what is the atomic weight of the element? Check from a Table of atomic weights and name the element. Can this element form a chloride with any other atom ratio?

2. If the atomic weight of oxygen were taken as 8.00 instead of 16.00 how would it change the atomic weights of sulphur, hydrogen and nickel?

3. Magnesium has three isotopes of masses 24.0, 25.0 and 26.0, the percentage abundance being 78, 10 and 12 respectively. Calculate the atomic weight of magnesium.

4. On electrolysis of an aqueous solution of curpric solution the following reaction takes place at the cathode: $Cu^{2+} + 2e \rightarrow Cu$
1.93 × 10^5 coulombs is needed to deposit one gram atomic weight of copper. Given the clue that an electron carries 1.60 × 10^{-19} coulombs calculate the number of atoms in one gram atomic weight of copper.
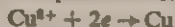
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Some Fundamental Physical Properties of Atoms and Molecules

We discuss in this Chapter some fundamental properties of atoms and molecules, that are consequences of the electronic configurations of the elements. Of these, ionisation potential, electron affinity, electronegativity are of vital importance for any discussion of variation in chemical properties of elements. A discussion of these three properties will be followed by a resume of ionic radii, atomic radii, covalent radii and van der Waals radii.

4.1. IONISATION POTENTIAL

If enough energy is supplied to an electron of a particular atom, it can be promoted to successively higher energy levels. If the supplied energy is large enough it may be possible to remove the electron completely from the pull of the positive nucleus. *The minimum energy required to remove an electron completely from a gaseous atomic species is called the first ionisation (energy) potential of the atom.*

$$\text{atom} + \text{ionisation energy} \rightarrow \text{unipositive ion} + \text{electron}$$
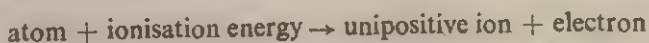
It is usually measured in electron volts, one electron volt (ev) being the energy gained by an electron falling through a potential difference of one volt (1 ev = 1.6×10^{-12}ergs). It is also often expressed in Kcal/mole (1 ev = 23.06 K cal/mole). A given element will have several ionisation potentials, one for each electron it has. Successive removal of electrons from an originally neutral atom gives the first, second, third, etc ionisation potentials.

A brief sketch of the experimental technique for determination of ionisation potentials may be enumerated. We know that gases conduct best at low pressures

and that a minimum voltage is required before conduction begins. This means that some minimum quantity of energy is required to produce ions from otherwise neutral atoms or molecules. The experimental set-up combines an electron source and a mass spectrometer. The electron source produces a beam of electrons whose energy can be regulated and measured. The electron beam is directed at a sample of a monatomic gas. (Diatomic molecules are to be atomised first, and then subjected to the electron beam). Positive ions formed in the process are detected in the mass spectrometer. The mass spectrometer can differentiate between ions with different charge/mass ratios. If a single monatomic gas of known atomic mass is used, the charge on each type of positive ion can be determined since all the ions have the same mass. It is, thus, possible to decide how many electrons the atom has lost in producing each different type of ion. As the energy of the bombarding electron beam is increased, the monatomic gas reaches an energy at which positive ions with a single positive charge appear in the mass spectrometer. The energy of this particular electron beam, which compels ionisation, corresponds to the first ionisation potential of the monatomic gas. Ionisation potentials of simple hydrogen-like ions can also be obtained simply by the calculation of transition energy between the ground state and the state at infinity (Chapter 1). With hydrogen atom there is only one ionisation potential. With helium atom there is a first ionisation potential associated with the loss of one electron and a second ionisation potential associated with the loss of a second electron. A list of the first ionisation potentials of different elements is given in Table 4.1.

The following factors influence the magnitude of the ionisation potentials: (1) the distance of the electron from the nucleus, (2) the charge on the nucleus (that is, atomic number), (3) the screening effect of the lower lying inner electrons and (4) overall charge on the ionising species.

(1) *The greater the distance of an electron from the positively charged nucleus of an element, the weaker will be the attraction and hence the lower the ionisation potential of that element.* If an atom is raised to an excited state by promoting one electron to a higher energy level, then that electron is farther from the nucleus and it is observed that this excited electron is more easily detached than when the electron is in its ground state.

(2) *The higher the charge on the nucleus the more difficult it is to remove an electron and hence the higher is the value of the ionisation potential.* In a group in the Periodic Table both the distance of the valence electrons from the nucleus and the nuclear charge increase with increasing atomic number. These factors will have opposing effects on the potential, although the distance factor seems to be more important. In a horizontal row (period) of elements, with increasing atomic number electrons are added to orbitals of the same principal quantum number. These electrons add little to the size of the atom, the increasing nuclear charge bringing about a contraction in size. In effect, therefore, *ionisation potential steadily increases along a period.*

(3) Electrons provide a screening effect on the nucleus. The outermost electrons are shielded from the nucleus by the inner electrons. The radial distribution functions of the *s*, *p* and *d* orbitals (Chapter 1) show that for the same

principal quantum number the s orbital is the most penetrating, next is the p orbital and least penetrating is the d-orbital. Screening efficiency falls off in the order $s>p>d$.

(4) *An increase in the overall charge on the ionising species e.g., M^+, M^{2+}, etc. will enormously influence the ionisation potential since electron withdrawal from a positively charged species is more difficult than from a neutral atom.*
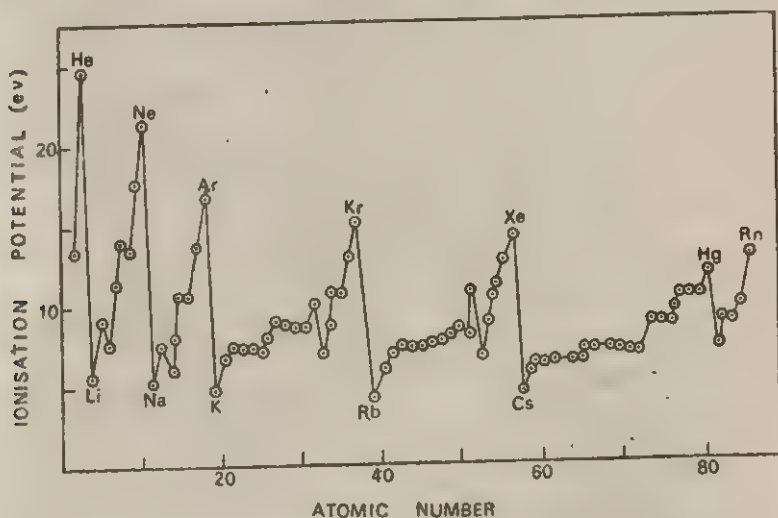
FIG. 4.1. First ionisation potentials as functions of atomic numbers

The first ionisation potentials of the elements vary with their positions in the Periodic Table (Fig. 4.1). In each period of the Table the noble gas has the highest value and the alkali metal the lowest value for the potential. Note that *the potentials of elements in a group gradually decrease with increasing atomic number,* as for example, in the alkalies:

Li	Na	K	Rb	Cs
5.39	5.14	4.34	4.18	3.89 (*ev*)

The low ionisation potentials indicate their great chemical activity and further point to the high degree of stability associated with noble gas electronic configuration. As we go from lithium ($1s^2 2s^1$) to neon ($1s^2 2s^2 2p^6$) the seven electrons, which are added, belong to the same principal quantum shell. Since the radial distribution functions of all the six p electrons are identical and since p electrons are poor shielders, the increased nuclear charge is heavily felt by the outermost electrons. Consequently the noble gases possess high ionisation potentials:

He	Ne	Ar	Kr	Xe
24.58	21.56	15.76	14.00	12.13 (*ev*)

The increase of the first ionisation potentials along a period is shown, for example, by the following series:

Li	Be	B	C	N	O	F
5.39	9.32	8.29	11.25	14.53	13.61	17.42 (*ev*)

Table 4.1. First Ionisation Potentials of Elements (ev)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 13.59																	He 24.58
Li 5.39	Be 9.32											B 8.30	C 11.26	N 14.53	O 13.61	F 17.42	Ne 21.56
Na 5.14	Mg 7.64											Al 5.98	Si 8.15	P 10.48	S 10.36	Cl 13.01	Ar 15.75
K 4.34	Ca 6.11	Sc 6.54	Ti 6.82	V 6.74	Cr 6.76	Mn 7.43	Fe 7.90	Co 7.86	Ni 7.63	Cu 7.72	Zn 9.39	Ga 6.00	Ge 7.88	As 9.81	Se 9.75	Br 11.84	Kr 14.00
Rb 4.18	Sr 5.69	Y 6.38	Zr 6.84	Nb 6.88	Mo 7.10	Tc 7.28	Ru 7.36	Rh 7.46	Pd 8.33	Ag 7.57	Cd 8.99	In 5.78	Sn 7.34	Sb 8.64	Te 9.01	I 10.45	Xe 12.13
Cs 3.89	Ba 5.21	La 5.61	Hf ...	Ta 7.88	W 7.98	Re 7.87	Os 8.7	Ir 9.0	Pt 9.0	Au 9.22	Hg 10.43	Tl 6.10	Pb 7.41	Bi 7.29	Po 8.43	At ...	Rn 10.75

The values for boron and oxygen are slightly lower than would be expected. Nitrogen has the configuration $1s^2 2s^2 2p^1_x 2p^1_y 2p^1_z$ and oxygen has $1s^2 2s^2 2p^2_x 2p^1_y 2p^1_z$. Oxygen has two electrons in the same orbital and the resulting repulsion between the two electrons is responsible for the drop in ionisation potential from nitrogen to oxygen. Another way of stating this will be that the half filled subshell in nitrogen is more stable. The drop from beryllium to boron is due to (1) the extra stability associated with a filled shell, or subshell ($1s^2 2s^2$ in Be) and (2) higher energy of the $2p$ electron in B ($1s^2 2s^2 2p^1$). Moreover an increase in atomic number (i.e., one more proton in the nucleus) also makes the ns^2 electrons more tightly bound.

It is also interesting to see that the potential of an alkaline earth metal is always greater than that of the preceding alkali metal. Compare K(4.34 ev) and Ca (6.11 ev); Rb(4.18ev) and Sr(5.69 ev); Cs(3.89 ev) and Ba(5.21 ev). Once again filled s sub-shells impart an extra stability.

A considerable difference exists between ionisation potentials of transition metals and those of non-transition elements. The difference obviously is to be related to the peculiar screening effect of the d orbitals. More of this appears in Part II.

When successive ionisation potentials of the same element are considered the effective charge becomes larger and the positive ions contract in size. These
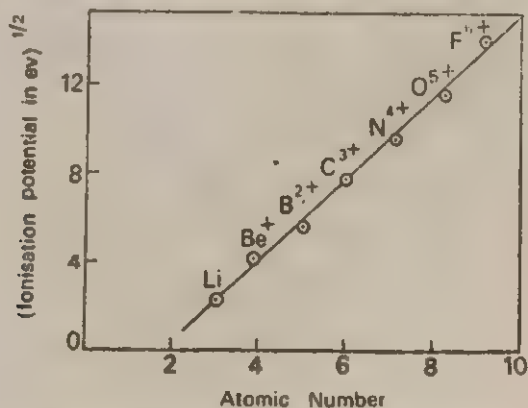
FIG. 4.2. Ionisation potentials of an isoelectronic
series of atoms and ions

two effects lead to a large increase in successive ionisation potentials. For example, the first, second and third ionisation potentials of magnesium are: 7.64, 15.03 and 80.12 ev respectively.

The combined effect of nuclear charge and overall charge on the ionisation potential of the charged species is remarkably shown by an examination of an isoelectronic series of atoms and ions. Consider the series:

Li	Be$^+$	B^{2+}	C^{3+}	N^{4+}	O^{5+}	F^{6+}
5.39	18.21	37.92	64.48	97.86	138.10	185.14 ev

These seven species all belong to different elements but all have the same electronic configuration $1s^2 2s^1$. However their nuclear charges are different (+ 3 for Li to

+ 9 for F+). If all these species lose one more electron all will move to the helium electronic configuration $1s^2$. Increasing nuclear charge and increasing overall charge together should make it harder for the species to ionise still further. Since both the factors increase from Li to F^{6+} it is expected that their ionisation potentials should also vary accordingly. The plot of the square roots of the ionisation potentials versus atomic number (nuclear charge) gives a straight line (Fig. 4.2).

For the general case of an electron moving around a nucleus of charge $+$ Ze the energy associated with a transition will be in accordance with equation (8) of Chapter 1:

$$E = \frac{2\pi^2 m Z^2 e^4}{h^2} \left(\frac{1}{n_I^2} - \frac{1}{n_{II}^2} \right) \quad (E = \text{I.P. when } n_{II} = \infty)$$

so that ionisation potential becomes proportional to the square of the nuclear charge, i.e., $E^{\frac{1}{2}}$ varies as Z.

4.2. ELECTRON AFFINITY

The electron affinity of an atom is defined as the energy liberated when a gaseous atom captures an electron.

atom + electron→uninegative ion + electron affinity

Evidently electron affinity is equal in magnitude to the ionisation energy of the species formed. The definition of electron affinity as the exothermicity of the electron capture reaction would lead to a negative sign according to our usual convention. But electron affinity is normally described with a positive sign. Negative electron affinities are known. These negative values indicate that the species concerned does not like to have any more electron.

Electron affinities are difficult to obtain. These are often obtained from indirect measurements: by analysis of Born-Haber energy cycles in which one step is electron capture or by the direct study of electron capture from heated filaments. In the latter method the number of neutral atoms, negative ions and electrons are determined with a mass spectrometer. This gives the standard free energy for the equilibrium $X + e \rightarrow X^-$. The free energy can be calculated from the temperature dependence of the equilibrium constant.

Some electron affinity values for different atoms are given in Table 4.2. The halogens have the highest electron affinities, although they do not show a monotonic (linear) decrease from fluorine to iodine. Their high values are indicative of their desire to attain stable noble gas configurations. Note that the alkali metals have very low electron affinities. This is in conformity with their ease of losing valence electron (low ionisation potential). Beryllium, magnesium and zinc also have small negative electron affinities. The reason for the negative values for the formation of O^{2-} and S^{2-} is that the second electron must be added to an already negative ion.

Electron affinity data on noble gases are not available. Complete lack of evidence for stable noble gas anions is sufficient proof of their low electron affinity. An electron, even if accepted by a noble gas atom, would have to go into an orbital in the next quantum shell (say for argon from $1s^2 2s^2 2p^6 3s^2 3p^6$ to $1s^2 2s^2 2p^6 3s^2 3p^6$

Table 4.2. Electron Affinities of Some Atoms

(For oxygen, sulphur and selenium values for X→X^{2-} are also included)

Atom	Electron affinity (ev)	Atom	Electron Affinity (ev)
H	0.747	S→S^{2-}	−3.91
F	3.45	Se	1.70
Cl	3.61	Se→Se^{2-}	−4.21
Br	3.36	Li	0.54
I	3.06	Na	0.74
O	1.47	K	0.70
O→O^{2-}	−7.41	Be	−0.60
C	1.25	Mg	−0.30
Si	1.63	B	0.20
N	−0.10	Al	0.60
P	0.70	Zn	−0.90
S	2.07		

$4s^1$), and presumably the nuclear charge is not high enough to hold an electron placed so far out.

The negative values of the second electron affinity for oxygen, sulphur may appear surprising in view of the existence of very stable metal oxides and sulphides. The answer to this is that ionisation potential and electron affinity are not the only factors that are responsible for compound formation. Ionic compounds, in particular, achieve a good deal of extra stability due to lattice energy, which arises out of close packing of oppositely charged ions in a crystalline lattice (Chapter 5).

4.3. ELECTRONEGATIVITY

In a compound the electron attracting powers of dissimilar atoms are different. *Pauling has defined electronegativity as the power of an atom in a molecule to attract electrons onto itself.* The reader must note that electron affinity and electronegativity are both index of electron attracting power but the former refers to an isolated atom and the latter to an atom in a compound.

Let us consider a pair of atoms, A and B, which combine to form a compound AB with a single bond between them. The two electrons making the single bond can assume three different positions as under:

$$A^+ \quad :B^- \qquad A \quad : \quad B \qquad A: \quad B$$
$$1 \qquad\qquad\qquad 2 \qquad\qquad\qquad 3$$
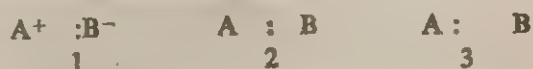
1. Both the electrons may reside in an orbital of atom B to form a negative B$^-$ and a positive ion A$^+$. In this case the electronegativity of B is far greater than that of A, and an ionic bond results (e.g. Na$^+$Cl$^-$).

2. The two electrons might be shared equally by overlap of orbitals of A and B. In this case, the electronegativities of A and B are equal, and a non-polar covalent bond is formed (eg : H_2, Cl_2).

3. The two electrons might be somewhat closer to A than to B, that is, a major share of the electron pair will reside on the A side of the overlapped orbitals. In this case, electronegativity of A is somewhat greater than that of B, and a polar covalent bond results (eg : $Cl\delta^- - H\delta^+$).

Several approaches have been proposed for a quantitative measure of electronegativity. Of these, those initiated by Pauling, Mulliken, and Allred and Rochow are important.

Whenever two or more atoms combine to form bonds there is liberation of energy. This energy is strictly called bond energy and must have a negative sign. Again this same magnitude of energy has to be supplied to break the bond. This latter is called bond dissociation energy and carries a positive sign. However bond dissociation energy and bond energy are used synonymously.

Pauling observed that *bond dissociation energy (defined as the energy absorbed per mole when a particular kind of bond is broken in the gas state, expressed in Kcal/ mole)* of a compound A—B (D_{A-B}) is always greater than the geometric mean of the bond dissociation energies of the molecules A—A and B—B. The geometric mean bond energy ($D_{AA} \cdot D_{BB}$)$^{\frac{1}{2}}$ is assumed to be the hypothetical bond dissociation energy of the compound A—B provided A—B has a purely non-polar covalent bond. The compound A—B will form a purely non-polar covalent bond provided both A and B possess similar electron attracting ability, otherwise the bond will develop a polar character eg. of the type $A^{\delta-}-B^{\delta+}$ showing some accumulation of negative and positive charges on A and B respectively. The difference $\triangle$ between the actual bond dissociation energy of A--B (D_{A-B}) and the hypothetical geometric mean bond dissociation energy, ($D_{AA} \cdot D_{BB}$)$^{\frac{1}{2}}$ is greater the greater the deviation of the bond A—B from non-polar covalent nature. Thus the greater the ionic character of the A—B bond the greater will be $\triangle$. This extra bond dissociation energy appearing in A—B molecule arises out of electrostatic attraction between A and B in the partial ionic form $A^{\delta-}-B^{\delta+}$. This extra energy possessed by a molecule with partial ionic character is called *ionic resonance energy* $\triangle$. This $\triangle$ has been used by Pauling as a measure of the difference in the electronegativities, x_A and x_B, of A and B. An empirical relation of the following type was set up:

$$x_A - x_B = \sqrt{\triangle/23.06} + \alpha = 0.208\sqrt{\triangle} + \alpha$$

Since bond dissociation energies are obtained in Kcal/mole, and since 1 $ev = 23.06$ Kcal/mole, the above relation expresses the square of the electronegativity difference in electron volts. α is an arbitrary constant which is nearly zero for elements other than C, N, O and F. Since $x_A - x_B$ is a difference, Pauling had to fix some point arbitrarily in his electronegativity scale. He used fluorine, the most electronegative element as the reference point with a value of 4.0. It is obvious that any scale of electronegativity must be used only in a qualitative sense.

The definition given by Mulliken is simple and allows some understanding of the term. He equated electronegativity to the average of the ionisation potential (I.P.) and electron affinity (E) of the element so that,

$$\text{electronegativity} = \frac{I.P. + E}{2}$$

This definition appears reasonable since the ultimate ability of an atom to attract shared electrons should be the mean of the quantities related to the power of the free atom to (a) hold on to its own electron ($= I.P.$) and (b) to attract additional electron ($= E$). If the energies of the two resonating structures $A^-B^+ \leftrightarrow A^+B^-$ are equal then we can write the following:

IP. of $B - E$ of $A = I.P.$ of $A - E$ of B

∴ I.P. of $A + E$ of $A = I.P.$ of $B + E$ of B

The above situation will prevail when the electronegativities of the two atoms are equal. But if A is more electronegative than B, then:

I.P. of $A + E$ of $A > I.P.$ of $B + E$ of B

These arguments support the Mulliken definition of electronegativity.

When ionisation potential and electron affinity are expressed in Kcal/mole, then the sum of the two has to be divided by a factor 125 in order to adjust the Mulliken value to the Pauling scale. On the other hand, when the quantities I.P. and E are expressed in electron volts, each one has to be divided by 3.15 before calculating the mean value. Mulliken's approach, although more straightforward, is of limited utility since electron affinities are not known except in a few cases.

Allred and Rochow started from the conception that an electron in a bond is attracted by one of the two nuclei of the diatomic molecule according to Coulombic law:

$$\text{Force} = \frac{Z^* e^2}{r^2}$$

where $Z^* = Z - \sigma$, Z being the nuclear charge and σ, the screening constant, Thus Z^* is the effective nuclear charge felt by an electron of the bond, and r is the mean distance from nucleus. Z^* is estimated from a set of shielding parameters set up by Slater and r is taken as the covalent radius of the atom. Such forces are calculated for different atoms and are plotted against Pauling electronegativities. From the slope and intercept of this line the following equation is derived by Allred and Rochow:

$$\text{Electronegativity} = 0.359 \frac{Z^*}{r^2} + 0.744$$

This equation thus brings the Allred-Rochow electronegativities close to Pauling scale. Thus Allred Rochow electronegativity is the electrostatic force experienced by the valence electrons due to the positive attraction of the mother nucleus.

A complete set of Pauling electronegativities is given in Table 4.3 for elements in their common oxidation states.

Table 4.3. Pauling Electronegativities (H = 2.1)

Li	Be											B	C	N	O	F
1.0	1.5											2.0	2.5	3.0	3.5	4.0
Na	Mg											Al	Si	P	S	Cl
0.9	1.2											1.5	1.8	2.1	2.5	3.0
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
0.8	1.0	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6	1.6	1.8	2.0	2.4	2.8
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.9	2.2	1.9	1.7	1.7	1.8	1.9	2.1	2.5
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
0.7	0.9	1.1-1.2	1.3	1.5	1.7	1.9	2.2	2.2	2.2	2.4	1.9	1.8	1.8	1.9	2.0	2.2
Fr	Ra	Ac	Th	Pa	U	Np										
0.7	0.9	1.1	1.3	1.5	1.7	1.3										

In a group with increasing size, the nucleus is removed farther and farther from the outermost (bonding) electrons. As a result the electron dragging power of the positively charged nucleus decreases with increasing atomic number in a group. On the other hand, along a period the effect of increasing number of protons in the nucleus outweighs the effect of addition of electrons in the same principal quantum shell. Since electrons are added to the same principal quantum shell no increase in size can take place. Instead a contraction occurs due to the enhanced dragging power of the nucleus as a result of increase in the number of protons. Hence *electronegativity falls with increase in atomic number in a group, and increases with increasing atomic number along a period.* Thus halogens are the most electronegative elements and the alkalies the least electronegative ones. *If there is an appreciable difference in the electronegativities of two elements a bond between them is likely to be ionic. If the individual electronegativities are high and the difference between them is small the bond is likely to be covalent* (Table 4.4). Electronegativity is also influenced by the oxidation state of an element: *the higher the oxidation state the greater will be the electronegativity.* Thus sulphur in SF_6 is surely more electronegative than the sulphur in SCl_2. Similarly quadrivalent nickel is more electronegative than bivalent nickel. That electronegativity varies with oxidation number is seen from the following data given by Pauling: Fe (II), 1.8; Fe (III), 1.9; Cu (I), 1.9; Cu (II) 2.0; Sn (II) 1.8; Sn (IV) 1.9 *ev*), etc.

Electronegativity seems to be influenced by the nature of hybridisation (Chapter 5) of the bonding atoms. Since *s* orbital is more penetrating than *p* orbital, therefore the greater the *s* character of the hybrid orbital the greater will be its electronegativity. The % *s* character in *sp*, *sp²* and *sp³* is 50, 33 and 25 respectively. Thus *sp* hybridised carbon in acetylene ($H-C \equiv C-H$) is more electronegative than *sp²* hybridised carbon in ethylene ($H_2C = CH_2$). The enhanced electronegativity of carbon of acetylene will draw major part of the electron density of the carbon-hydrogen bond, thus making acetylene somewhat acidic in nature.

Table 4.4. Electronegativity and Bond Type

Electronegativity A	B	Interaction	Bond type
Low	High	Electron transfer	ionic
High	High	Electron pair sharing	covalent
Low	Low	Free electron sea or collective electron orbitals (like molecular orbitals)	metallic

That the greater the electronegativity difference between the bonding elements the greater is the ionic character of the bond is shown in Fig. 4.3.

Per cent ionic characters of the halogen hydrides and the electronegativity differences between the hydrogen and the respective halogens are given below.

Dipole moment and bond length allow us to make a rough estimate of the per cent ionic character (Section 5.4).

Hydride	HF	HCl	HBr	HI
Electronegativity difference	1.9	0.9	0.7	0.4
Per cent ionic character	46	17	12	5
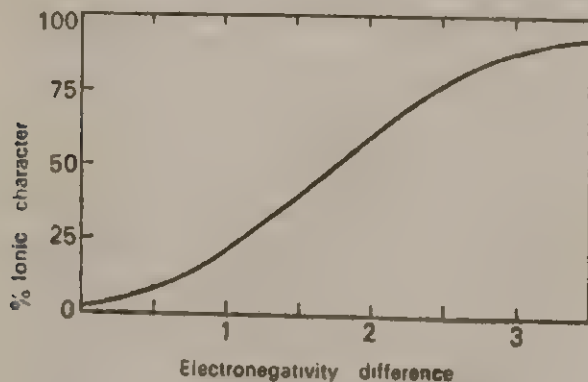
FIG. 4.3. Variation of percent ionic character with electronegativity difference

4.4. IONIC RADII

Ionic radii correspond to the radii of ions in ionic crystals. Isolated ions are difficult to obtain for physical studies and such isolated ions will be very much different from ions in crystals. *Chemists are interested in ionic radii such that the sum of two radii is equal to the equilibrium internuclear distance between the corresponding ions in a crystal.* Physical measurements, such as X-ray, on ionic crystals provide data on the internuclear distance of the two opposite ions of the ionic compound. Thus rubidium ion and iodide ion are separated by a distance of 3.64 A, and potassium and bromide ions by 3.29 A. Unless one has a knowledge of the ionic radius of one of the ions of each of the above pairs, the above X-ray data are simply useless. In order to solve such difficulties lithium iodide crystals were examined. Lithium ion being the smallest possible mono-positive metal ion in the Periodic Table, it was reasonable to assume that in lithium iodide, the very much larger iodide ions (Li^+, 0.60 A; I^-, 2.16 A) will be touching each other in the crystal lattice. The half of the iodide-iodide internuclear distance in lithium iodide, therefore, provides a reasonable value for the ionic radius of the iodide ion. Thus fixing a standard at iodide ion, the ionic radius of rubidium ion in rubidium iodide could be calculated. Suitable choice of ionic compounds, and measurements on them have provided a long list of ionic radii.

Pauling also brought in some semitheoretical approach in this area. He assumed that the size of an ion is dictated by the distribution of the outermost electrons. This distribution of outermost electrons again depends on the nuclear attraction. Since the inner electrons screen the nucleus, the nuclear attraction on the

outermost electrons will be a function of an effective nuclear charge Z^*, rather than the nuclear charge Z. On this basis the ionic radius, r, of the ion is given by

$$r = C_n/Z^*$$

with C_n being a constant determined by the total number of electrons in the noble gas configuration attained. For isoelectronic ions in chemical combination (eg: NaF) the constant term is the same for both the ions. Therefore

$$\frac{r(Na^+)}{r(F^-)} = \frac{Z^*(F^-)}{Z^*(Na^+)}$$

The effective nuclear charge (actual nuclear charge minus the screening effect of the other electrons in the ion) for sodium ion is 6.48 and that for fluoride ion is 4.48, so that

$$\frac{r(Na^+)}{r(F^-)} = \frac{4.48}{6.48}$$

The experimentally obtained internuclear distance in sodium fluoride is 2.31 A, so that the above relation yields the ionic radii values for Na^+ and F^- as 0.95 A and 1.36 A respectively.

4.5. ATOMIC AND COVALENT RADII

These are often used synonymously. Our knowledge of the electrons has shown that they can be discovered almost anywhere around the nucleus, although there is a most probable distance from the nucleus where they are most likely to be found. It is therefore not possible to define precisely the contour of an isolated atom. When atoms approach each other in solid state, they take up equilibrium positions such that repulsions between positive nuclei is balanced by attractive forces of chemical bonds. Under such conditions atoms assume finite size and atomic radii become half the internuclear distance separating the like atoms. Physical measurements again furnish data for interatomic distances in free elements (e.g: Na, K, C) and diatomic molecules (F_2, Cl_2). If the atoms of metals are assumed to be spherical, a radius can be calculated for each atom in the metallic crystal provided we know the density of the metal, the nature of the unit cell and the number of atoms in the unit cell. The calculation of the atomic radii of metals is further based on the assumption that the metals form closest packed structures. Atomic radii of metals are also often termed as metallic radii.

In a homonuclear diatomic molecule (eg : F_2, Cl_2) there is a covalent bond holding together two atoms. The internuclear distance in such molecules is called the bond length. One half of this bond length is called the covalent radius of the element. Thus the bond length of hydrogen molecule being 0.74 A, the covalent radius of hydrogen atom is 0.37 A. The bond length of a covalent diatomic heteronuclear molecule can be calculated by adding the relevant covalent radii. The covalent radii of hydrogen and chlorine are 0.37 A and 0.99 A respectively so that the bond length of HCl is given by 1.36 A, in rough agreement with the experimental value of 1.27 A. This covalent radius (0.37 A) of hydrogen does not truly hold when

hydrogen is bonded to other atoms. In such cases 0.28 A is taken as the covalent radius of hydrogen, which is obtained by subtracting the covalent radius of X from X—H bond lengths (eg : radius for H in HCl : 1.27—0.99 = 0.28 A). The carbon-carbon distance in diamond is 1.54 A so that the atomic radius of carbon is 0.77 A. Similar measurements in pure silicon gives an atomic radius of 1.17 A. In a compound containing carbon and silicon single bond the C—Si bond length should be 1.94 A. Tetramethylsilane $(CH_3)_4Si$ has C—Si bond length of 1.93 A.

It is to be noted that covalent radius of an element will change with a change in its covalent bonding pattern. A 'C—C' single bond radius (0.77A) is different from C = C double bond radius (0.66 A), which again is different from a C ≡ C triple bond radius (0.602 A). *It may be remarked that as the bond length decreases with multiple bonding, the bond strength increases.* Supporting evidence is the increase in bond energies in Kcal/mole (kJ/mole) with multiple bonding, for example:

$$
\begin{array}{llllll}
C - C, & 83\ (347), & N - N, & 38\ (169) & C - O, & 84\ (351) \\
C = C, & 143\ (578) & N \equiv N, & 225\ (941) & C = O, & 173\ (724) \\
C \equiv C & 196\ (820) & & & &
\end{array}
$$

For elements which do not form diatomic molecules with single bonds (eg: N_2 has N ≡ N) indirect methods are used to evaluate their single bond covalent radii. Measurements on methylamine $H_3C—NH_2$ gives a C—N bond length as 1.47 A. Subtracting from this bond length the C—C covalent radius (0.77 A) we have nitrogen single bond covalent radius as 0.70 A.

The concept of covalent radii is quite useful so long as predominantly covalent molecules are concerned. However they are of little value when the compounds are predominantly ionic. Multiple bonding between two atoms is indicated when the measured bond length is considerably shorter than the sum of the two single bond covalent raddi.

4.6. VAN DER WAALS RADII

When two atoms are bonded together through sharing of an electron-pair the bond is called a covalent bond. The forces giving rise to a covalent bond do not extend beyond the limits of the molecule. However a far weaker force operates between covalent molecules bringing them close enough to contact position. In such situation two kinds of internuclear distances can be detected. The first is the internuclear distance between the two nuclei forming the electron pair-covalent bond. This distance is the covalent diameter or double the covalent radius. Besides this, there is another internuclear distance between two nearest nuclei belonging to two nearest molecules. This particular internuclear distance is called the van
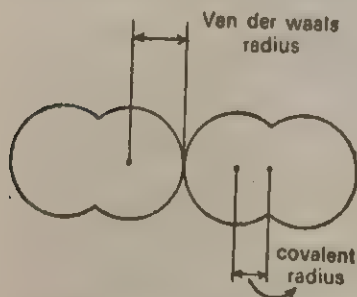
FIG. 4.4. Covalent radius and van der Waals radius

der Waals diameter of the atom and half this internuclear separation is the van der Waals radius of the atom (Fig. 4.4). For further details see Chapter 5.

4.7. COMPARISON OF RADII

A list of chosen ionic and atomic (covalent) radii is given in Table 4.5. The following generalisations concerning the sizes of ions can be advanced.

1. A series of isoelectronic ions and atoms such as O^{2-}, F^-, Ne, Na^+, Mg^{2+} and Al^{3+} show a steady decrease in radius (1.40, 1.36, 1.12, 0.95, 0.65 and 0.52 A respectively) with increasing nuclear charge (8, 9, 10, 11, 12 and 13 respectively). *The increased nuclear charge tends to pull the outer electrons close to the nucleus.*

2. *The radii of negative ions are larger than those of the corresponding atoms* (Cl, 0.99 A and Cl^-, 1.81 A). As there are not enough protons in the nucleus to control the electrons, the most probable distance of the electrons from the nucleus increases.

3. *Positive ions are considerably smaller than the atoms from which they are derived.* A positive ion has a surplus nuclear charge which can squeeze the electron shells (K, 2.31 A and K^+, 1.33A)

4. *Within a group of regular elements both atomic radii and ionic radii increase with increasing atomic number.* This is due to addition of new quantum shells. Increased nuclear charge cannot force contraction of size since new principal shells are added.

5. *Along a period the atomic (covalent) radius falls off with increasing atomic number.* Increasing nuclear charge now becomes significant since electron addition to the same principal quantum shell cannot add to the size. Watch the following series:

Li	Be	B	C	N	O	F
1.52	1.11	0.88	0.77	0.70	0.66	0.64 A

While the atomic (covalent) radius of fluorine is 0.64 A that of neon is 1.12 A. There is nothing surprising here. The covalent radius of fluorine is half the inter-nuclear distance between the two covalently bonded atoms in F_2. Since neon is monatomic there is no covalent interaction. Hence its atomic radius really is almost its van der Waals radius.

In the context of these general rules the reader may have a critical look at the transition elements. Let us compare aluminium ($1s^2 2s^2 2p^6 3s^2 3p^1$) with gallium ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$) in the same group. The atomic number has increased from 13 to 31. Being members of the same vertical group gallium is expected to have an increase in atomic radius over that of aluminium. However the results show a different story (Ga, 1.26 A; Al, 1.26 A). The explanation lies in appreciating the role of d orbital electrons. Calcium ($1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$) expectedly has an atomic radius (1.97 A) larger than that (1.60 A) of magnesium ($1s^2 2s^2 2p^6 3s^2$). After calcium the d level electrons continue to be added. The radial distribution functions show that $3d$ electrons do not extend beyond the $4s$ electrons. Therefore whatever number of such $3d$ electrons are added to the calcium structure

6

Table 4.5. Atomic and Ionic Radii

Atom	Atomic Radius (A)	Ions	Ionic Radius (A)
H	0.37 (0.28)	H-	2.08
He	0.93	...	...
Li	1.52	Li+	0.60
Be	1.11	Be²+	0.31
B	0.88	B³+	0.20
C	0.77		
N	0.70	N³-	1.71
O	0.66	O²-	1.40
F	0.64	F+	1.36
Ne	1.12	...	...
Na	1.86	Na+	0.95
Mg	1.60	Mg²+	0.65
Al	1.26	Al³+	0.52
Si	1.17	Si⁴+	0.39
P	1.10	P⁵+	0.34
S	1.04	S²-	1.84
Cl	0.99	Cl-	1.81
Ar	1.54	...	...
K	2.31	K+	1.33
Ca	1.97	Ca²+	0.99
Br	1.14	Br-	1.95
Rb	2.44	Rb+	1.48
Sr	2.15	Sr²+	1.10
I	1.33	I-	2.16
Cs	2.62	Cs+	1.69
Ba	2.17	Ba²+	1.29

they cannot increase the size, instead the increasing nuclear charge coupled with poor screening effect of d-electrons brings about a slow contraction in size. This slow contraction in size is also reflected in their ionisation potentials, which either show a slight increase or remain within a short range. (Sections 10.11.2 and 22.2.1).

Alongwith this discussion it is necessary to impress that such contraction is even more important in the series of lanthanides (atomic number 57 to 71) which have their extra electrons occupying an inner $4f$ shell. The result is obvious. These electrons hardly add to their size, instead the nuclear charges pull very effectively all the electron shells, thus leading to lanthanide contraction. The poor shielding capability of d and f electrons can hardly cope with the increasing nuclear charge.

Some van der Waals radii are shown in Table 4.6. The van der Waals' radii are often close to the ionic radii of the corresponding anions. The only exception is the hydride ion (2.08 A). The hydride ion seems to be much too large compared to the isoelectronic helium (van der Waals' radius, 1.2A). But we have to

remember that a H^- anion has half the nuclear charge of helium and furthermore the two s electrons being good shielders, protect each other to a large degree from the pull of the nuclear charge, so that the electron orbitals remain more spread out.

Table 4.6. Covalent, Ionic and van der Waals Radii (A)

Atom	Covalent Radius	Ionic Radius (A)	van der Waals radius (A)
H	0.37 (0.28)	2.08 (H^-)	1.20
O	0.66	1.40 (O^{--})	1.40
F	0.64	1.36 (F^-)	1.35
S	1.04	1.84 (S^{--})	1.85
Cl	0.99	1.81 (Cl^-)	1.80
Br	1.11	1.95 (Br^-)	1.95
I	1.28	2.16 (I^-)	2.15

STUDY QUESTIONS

1. The ionisation potential of Rb is 4.18 ev. When its $5s$ electron is excited successively to $5p$, $5d$, $5f$ and $5g$ levels the potential value decreases to 2.60, 0.99, 0.55 and 0.54 ev. Comment. Do you think this is a general case?

2. A student states the sizes of atoms decrease along a period but increase along a group. Do you agree?

3. The first ionisation potential of sodium is the same as the electron affinity of Na^+ ion. Comment.

4. Support or contradict the statement that the second ionisation potential of an atom cannot be equal to or smaller than the first ionisation potential.

5. What is the difference between electron affinity and electronegativity? How do these two properties help us in predicting the ionic nature of compounds?

6. Arrange the following bonds in an expected order of increasing ionic character: B—O, C—O, Cl—O, F—O, N—O, H—O, Na—O.

7. Using the atomic radii in Table 4.5 calculate the interatomic distances in CCl_4, $SiCl_4$, $LiCl$ and $NaCl$. Compare your results with the experimental values given in parentheses: For Li and Na use as atomic radii half the metal-metal interatomic distances Li (1.57A) and Na (1.85 A). CCl_4 (1.77), $SiCl_4$ (2.01), $LiCl$ (2.57) and $NaCl$ (2.81). Comment on the results.

8. The ionic radius of Cl^- is greater than the mean of the radii of F^- and Br^- whereas that of Br^- is less than the mean of the radii of Cl^- and I^-. Discuss.

9. Compare the sizes of a neutral atom and its negative ion. Explain the extraordinary difference in size of the hydrogen atom (0.37 A) and H^+ ion ($\sim 10^{-12}$ A).

10. Compare the ionic radii of Na^+, Mg^{2+} and of S^{2-} and Cl^-.

11. The successive ionisation potentials of boron are 8.29, 25.15, 37.92, 259.3 ev. Why the fourth potential is so high compared to the first three?

12. A study of the electron affinities of Na and H would militate against the formation of sodium hydride with hydrogen as the anion. How do you reconcile?

13. What evidence do you have to substantiate that the electrons belonging to an atom possess different energies?

14. What do you mean by the terms (i) covalent radius (ii) ionic radius? How do the covalent and the ionic radii vary along a group and along a period of the periodic table? What are the factors involved in such variations?

15. Explain which one of the following pairs will have the larger radius? (a) H, H^+ (b) H, H^- (c) Na^+, Cs^+ (d) O, O^{2-}

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The Nature of the Chemical Bond

The nature of the chemical bond forms the subject matter of this Chapter. We will define *a chemical bond as the force holding together two atoms or groups of atoms forming an aggregate of ions, or molecular species such that there occurs a lowering of energy.* Such definition permits us to discuss chemical bonds under the following three classes:

1. The ionic bond (also called electrovalent or electrostatic bond), 2. The covalent bond and 3. The metallic bond.

It will be proper to warn at the outset that these three bonds represent only three extreme types of forces between atoms. There will be many chemical compounds whose properties would indicate bonds of intermediate types. The discussion on the above bond types will be followed by a short resume on the various intermolecular forces, often expressed as van der Waals forces.

5.1. THE IONIC BOND

It is well known that sodium and chlorine react vigorously to yield crystals of sodium chloride. Crystallographic studies have shown that there is no discrete NaCl molecule in the crystal lattice; instead each sodium ion (Na^+) is surrounded by six chloride ions (Cl^-) and vice versa. This packing of two ions is repeated throughout in a non-ending pattern. The two oppositely charged ions are held together by means of electrostatic forces of attraction. Each neutral sodium atom Na° loses one electron to form a unipositive sodium ion (Na^+). Similarly a neutral chlorine atom (Cl°) gains one electron to form a uninegative chloride ion (Cl^-). The two ions Na^+ and Cl^- then build up a close packed type ionic crystal structure. Conceptually we find a transfer of electron from sodium atom to the chlorine atom:

$$Na^\circ \rightarrow Na^+ + e; Cl^\circ + e \rightarrow Cl^-; Na^+ + Cl^- \rightarrow NaCl$$

Ionic bonds are thus electrostatic forces that bind together oppositely charged ions formed by the transfer of electron (s) from an electropositive metal to an electronegative non-metal atom.

Let us now examine the motive of the above two elements behind the reaction. An examination of the electronic configuration of the elements and ions shows that both the ions have attained noble gas configuration.

Na ⇅ ⇅ ⇅ ⇅ ⇅ ↑   ; Na⁺ ⇅ ⇅ ⇅ ⇅ ⇅ (like Ne)
    1s 2s 2p 2p 2p 3s   1s 2s 2p 2p 2p

Cl ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ↑
    1s 2s 2p 2p 2p 3s 3p 3p 3p

Cl⁻ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ (like Ar)
    1s 2s 2p 2p 2p 3s 3p 3p 3p
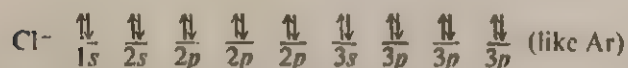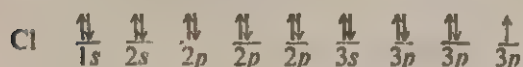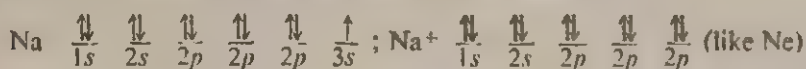
The noble gas elements have filled subshells, and their chemical inertness points to the stability of their electronic configurations. The truth of this is strikingly shown by their high ionisation potentials and very poor electron affinities. *Attainment of stable noble gas electronic configuration is thus the clue to chemical reactions.* Such conclusion helps us to predict which elements are most likely to form ionic compounds. The elements which have low ionisation potentials are the best candidates for forming positive ions (cations). Similarly the elements which have high electron affinity are most likely to form negative ions (anions). Factors that influence ionisation potential, electron affinity and electronegativity also influence the formation of ionic compounds. It is possible to draw the following conclusions:

(a) The lower the charge on the cation the better is the chance that an ionic compound will be formed. The lower the charge on the cation the lower is the ionisation potential.

(b) The formation of ionic compounds is favoured by large size of the metal atom or ion since an increase in size is associated with a decrease in ionisation potential.

(c) Small size and low charge on the anion will favour ionic compounds because these factors are associated with increasing electron affinity and electronegativity.

The above discussion gives us a rough guide as to when to expect an ionic compound. Unexpected results are sometimes observed. For instance, the second electron affinity of oxygen is negative, yet it forms stable, ionic compounds with alkalies or alkaline earths. Clearly there must be other factors which play significant roles in the formation of ionic compounds.

5.1.1. Lattice Energy. Mere formation of oppositely charged ions does not lead to an ionic compound. In an idealised ionic compound there is considerable electrostatic force operating between the cations and anions, considered to be hard spheres. When these cations and anions are brought together in large and equal numbers they will arrange themselves in a regular pattern so as to attain a close packed type structure. While attaining such structure energy is liberated and thus

the system gets stabilised. *The energy liberated when the ionic crystal lattice is formed from an assembly of ions is called the lattice energy.* Conversely work has to be done on the ionic crystal to disperse the crystal into an assembly of widely separated ions.

The elementary physical picture of ionic compounds will indicate that alongside the attractive force between a cation and an anion there will also exist a repulsive force between them due to close approach of their electron shells. At equilibrium the ions will give rise to a close packed type system with the ions at a distance apart corresponding to their characteristic ionic radii.

The electrostatic potential energy of a pair of ions considered as point charges Z^+e and Z^-e at a distance r is given by

$$u = Z^+Z^-e^2/r$$

In a crystal lattice, however, we have to take account of mutual potential energies of all the charges in the structure. The electrostatic potential energy per pair of ions is:

$u = AZ^+Z^-e^2/r$; for univalent ions (carrying $+e$ and $-e$ charges) $u = -Ae^2/r$ where A is a numerical constant called Madelung constant. This constant is dependent on the geometry of the crystal lattice and its evaluation is not simple.

The repulsive force is represented by a term of the type $B \exp(-r/\rho)$ where B and ρ are constants for any one crystal. The lattice energy then takes the form:

$$u = -Ae^2/r + B \exp(-r/\rho)$$

B can be eliminated by setting the condition that the equilibrium distance r_0 between adjacent ions is that which makes the potential energy a minimum. Then,

$$\left(\frac{du}{dr}\right)_{r=r_0} = \frac{Ae^2}{r^2} - \frac{B}{\rho} \exp(-r/\rho) = 0$$

$$\therefore B \exp(-r_0/\rho) = Ae^2\rho/r_0^2$$

so that $(u)_{r=r_0} \qquad = -\frac{Ae^2}{r_0}\left(1 - \frac{\rho}{r_0}\right)$

The value of ρ is obtained from compressibility measurements while r_0 is found out from X-ray crystallographic measurements. It is also seen that a small value of ρ/r_0 represents a rapid variation of the repulsive force with distance and consequently a small compressibility. An appreciation of the variation of lattice energies of alkali halides can be made from the following Table 5.1. Note that with increase in the $A-X$ distance the lattice energy gradually falls off in a related series of alkali halides.

Table 5.1. Lattice Energies of some Alkali Halides

Alkali halide	A—X distance (A)	Calculated lattice energy (Kcal/mole) (kJ/mole)	Lattice energy from Born-Haber cycle (Kcal/mole) (kJ/mole)
LiF	2.01	−254 (−1062)	−244 (−1021)
LiCl	2.57	−196 (− 820)	−202 (− 845)
LiBr	2.75	−184 (− 770)	−192 (− 803)
LiI	3.00	−169 (− 707)	−180 (− 753)
CsF	3.00	−175 (− 732)	−173 (− 724)
CsCl	3.56	−150 (− 627)	−158 (− 661)
CsBr	3.71	−143 (− 598)	−150 (− 627)
CsI	3.95	−135 (− 565)	−145 (− 606)

kJ/mole = Kcal/mole × 4.184

5.1.2. The Born-Haber Cycle. Although lattice energy can be calculated from the relation given above, indirect estimates of the lattice energies are commonly made from what is known as Born-Haber Cycle of formation of an ionic compound.

Let us take one gm. molecule of sodium chloride in the crystalline state. By expending an amount of energy equal to the lattice energy of sodium chloride, $-U_{NaCl}$ the compound can be converted into a gas of ions Na^+ and Cl^-. Na^+ can be converted to Na atom by the recovery of an energy corresponding to the first ionisation potential (I_{Na}) of sodium. On the other hand, expending an amount of energy equivalent to the electron affinity (E_{Cl}) of chlorine atom will convert Cl^- to Cl atom. If the gaseous sodium atom is allowed to condense to solid sodium atom. an energy S_{Na} (− heat of sublimation) will be recovered. Similarly for chlorine atom $\frac{1}{2}D_{Cl}$ (D = heat of dissociation of chlorine per gram molecule) energy will be recovered. Finally by allowing the solid sodium atom to react with chlorine atom we get the heat of formation, of sodium chloride Q_{NaCl}. During the full operation of this cycle total energy interchange will be zero. Therefore we have:

Fio. 5.1, Born-Haber cycle applied to sodium chloride

$$-U_{NaCl} + E_{Cl} - I_{Na} - S_{Na} - \tfrac{1}{2}D_{Cl} - Q_{NaCl} = 0$$
$$\therefore U_{NaCl} = E - I_{Na} - S_{Na} - \tfrac{1}{2}D_{Cl} - Q_{NaCl}$$

All the quantities on the right hand side being measurable the lattice energy of NaCl can be calculated:

$U_{NaCl} = 85.8 - 117.9 - 26.0 - 28.8 - 98.3 = -185.2$ Kcal/mole. Values calculated by the use of such Born-Haber cycle for some selected halides are included in Table 5.1. It will be noted that agreement with calculated values is satisfactory.

. Thus, we see that the lattice energy, which is a measure of the stability of an ionic compound depends also on factors other than ionisation potential and electron affinity.

5.1.3. Solvation Energy. When a cation or an anion in the gaseous state reacts with a solvent in the liquid state, energy is liberated. This liberated energy is termed solvation energy. When the solvent is water the liberated energy is called hydration energy:

$$Z^{\pm X} (g) + H_2O (l) \rightarrow Z^{\pm X} (aq) + \text{hydration energy}$$

Water is a polar solvent (each hydrogen is δ^+ while each oxygen is δ^{--}). A gaseous cation is attracted by the negative oxygen ends of the water molecules while the anion is attracted by the hydrogen ends. The greater the charge/surface area i.e. the charge density of the ion the greater will be the interaction i.e. the greater will be the amount of energy liberated. This explains why Li^+ has a higher solvation energy than Na^+ or K^+. Again Mg^{2+} has a higher hydration energy than Ba^{2+} or Li^+. For the same reason hydration energy decreases from F^- to I^- ion.

Interestingly there is a considerable difference in the hydration energies of F^- and K^+ ions (Table 5.2), although they have the same ionic radius ($\simeq 1.36A$). This is due to the fact that F^- interacts with the small hydrogen atom (with δ^+ charge) while K^+ ion has to interact with the much larger oxygen atom (with δ^{--}). More hydrogen atoms can get around a F^- ion compared to oxygen atoms around the K^+ ion.

Table 5.2 Hydration energy of some common ions

Ion	Hydration energy	Ion	Hydration energy
Li^+	−124.4 Kcal/mole	F^-	− 121 KCal/mole
Na^+	− 97.0	Cl^-	− 87.0
K^+	− 77.0	Br^-	− 80.0
Mg^{2+}	−459.0	I^-	− 70.0
Ba^{2+}	−325.0	ClO_4^-	− 57.0

5.1.4. Properties Associated with Ionic Bond

1. Ionic crystal lattice is built up of oppositely charged ions.

2. Since electrostatic forces of attraction are omnidirectional i.e. extend in all directions each ion tends to drag as many of opposite kind around itself. A non-ending array of alternate positive and negative ions exists. Hence no isolated discrete molecule exists in the crystal lattice; instead 'giant' 'molecules' are formed. Ionic bonds are non-directional.

3. Ionic compounds are hard, and have high melting points and boiling points. This is because strong electrostatic forces have to be overcome in order to provide the necessary freedom of movement that characterises a liquid state.

4. Ionic compounds are soluble in polar solvents and insoluble in non-polar solvents. When an ionic compound is dissolved the crystal lattice is ruptured and the ions are held further apart in solution than in the crystal. During the

interaction of ionic compound with solvent, the lattice energy is lost but a solvation energy is gained due to the ions getting solvated. The negative end of a dipolar solvent molecule, attracts the cation and the positive end faces the anions. A polar solvent like water can penetrate the crystal lattice of an ionic compound and can effect dissolution. The solvent character is decided by the dielectric constant of the solvent. and the higher the dielectric constant the better it is as a solvent for ionic compounds. Conversely a non-polar solvent does not possess the necessary dipoles to initiate dissolution of an ionic compound. It has a low dielectric constant. For further discussion see Chapter 9.

5. Ionic compounds are conductors in fused state or in solution. In solid crystalline state such compounds are only poor conductors. In fused state an ionic compound is composed of ions which are not confined to fixed positions as in the crystal lattice. The freely moving ions can therefore permit electric conductance.

6. The reactions of ionic compounds are reactions of their ions and these are instantaneous in solution. Common precipitation reactions used in analysis belong to the class of ionic reactions.

5.2. THE COVALENT BOND

It is easy to have an understanding of an ionic bond which is formed as a result of electrostatic attraction between oppositely charged ions. Conceptually it is, however, much more difficult to gain an understanding of covalent bonding. It is unreasonable to suppose that the bond holding identical non-metal atoms to each other, as in H_2 or F_2 molecule, could be formed in the way sodium chloride is formed. Electron transfer seems more reasonable when two atoms with widely different electron affinity, such as hydrogen and fluorine, combine to form the compound HF. The properties of HF, however, differ widely from those characteristic of ionic compounds. Hydrofluoric acid is a non-conductor of electricity, is low boiling etc. Lewis suggested that such non-ionic molecular compounds (H_2, F_2, HF etc) are formed as a result of sharing of electrons between atoms whereby each atom can attain a noble gas configuration (that is either two electrons as in Helium, or an octet in the outermost shell like the other noble gases). *A covalent bond may be defined as a force holding together atoms through sharing of electrons.*

5.2.1. Lewis Representation of Covalent Compounds. The hydrogen atom has the electronic configuration:

$$H \; 1s^1 \text{ or } \underset{1s}{\uparrow} \text{ or } H \cdot$$

The H represents the nucleus and the dot represents the one valence electron outside that nucleus. When two such atoms combine to form a diatomic molecule the representation used is:

$$H : H \quad \text{or} \quad H - H$$

The two dots or the line (dash) between the two hydrogen atoms represents the covalent bond that holds the molecule together. Similarly the combination between hydrogen and fluorine atoms may be represented as:

$$\text{H} \cdot + \overset{\times\ \times}{\underset{\times\ \times}{\times \text{F} \times}} \longrightarrow \text{H} \cdot \overset{\vee\ \times}{\underset{\vee\ \vee}{\times \text{F} \times}} \quad \text{or simply as H—F}$$

The line joining the two hydrogen atoms in H_2 molecule or one hydrogen and one fluorine in HF molecule does not mean that the two electrons forming the covalent bond are located at a fixed position between the two nuclei. In reality at any instant the electrons may be located at any of the various points between or around the two nuclei, although on an average there is a much greater probability of finding the electrons between the two nuclei than at the far ends of the molecule. A point that is conveyed by the line or dash in H_2 or in HF is that there is a two-electron single bond between the atoms and that each of the atoms contribute one electron towards the bond.

It is not essential that for covalent bonding the partners need to contribute equally. For example in the compound $BF_3.NH_3$ both the electrons come from ammonia. Such a bond is called a coordinate bond and is represented by an arrow to draw a distinction from the equally contributed two-electron single bond. Here NH_3 is a *donor* while BF_3 is an *acceptor*.

$$
\begin{array}{ccc}
\text{F} & \text{H} & \quad\quad \text{F} \quad\ \text{H} \\
| & | & \\
\text{F}-\text{B} + : \text{N}-\text{H} & \rightarrow & \text{F}-\text{B} \leftarrow \text{N}-\text{H} \\
| & | & \\
\text{F} & \text{H} & \quad\quad \text{F} \quad\ \text{H}
\end{array}
$$
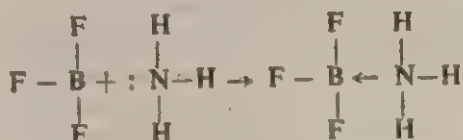
It should be made clear, however, that once a coordinate bond is formed it cannot be distinguished from ordinary single covalent bonds. The arrow still serves as a mental aid and will be used whenever we need to.

Lewis representation may be extended to cover multiple covalent bonds also. Let us take the examples of carbon dioxide and ethylene C_2H_4. With the following notations

$$\cdot \overset{\cdot}{\underset{\cdot}{\text{C}}} \cdot \quad\quad \overset{\vee\ \vee}{\underset{\vee\ \times}{\times \text{O} \times}} \quad \text{and} \quad |\text{*H}$$

we can write the following structures

$$\overset{\times}{\underset{\vee\ \times}{\times \text{O} \times}} \quad \cdot \overset{\cdot}{\text{C}} \cdot \quad \overset{\vee\times}{\underset{\times}{\times \text{O} \times}} \quad \text{or} \quad \overset{\times}{\underset{\vee\times}{\times \text{O}}}-\overset{\cdot}{\text{C}}-\overset{\times\vee}{\underset{\times}{\text{O} \times}} \ ; \ \text{H}\vee \quad \cdot\overset{\cdot}{\text{C}}\cdot \quad \cdot\overset{\cdot}{\text{C}}\cdot \quad \times\text{H} \quad \text{or} \quad \text{H}-\overset{\text{H}}{\underset{\cdot}{\text{C}}}-\overset{\text{H}}{\underset{\cdot}{\text{C}}}-\text{H}$$
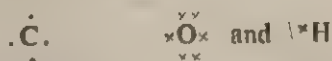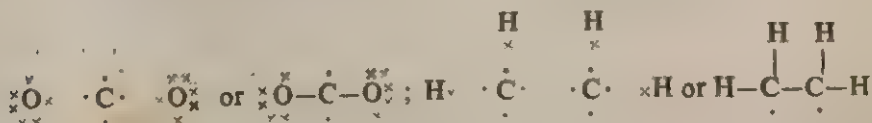
Unfortunately none of the structures allows noble gas (octet) configuration to oxygen or to carbon. However the octet rule can be most simply satisfied if a

second covalent bond is formed between carbon and oxygen in CO_2, and between the carbons in C_2H_4.
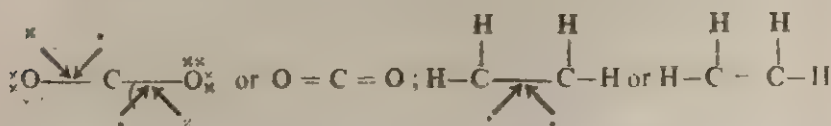
5.2.2. Valence Bond (VB) Theory of Covalent Bond.

We have so far not attempted to answer the logical question as to why at all sharing of electrons gives rise to the formation of a stable bond. The exact answer lies in quantum mechanics. We will endeavour to offer an explanation in popular language.

Let us consider the covalent bonding in the diatomic hydrogen molecule. Each hydrogen atom consists of a one-proton nucleus and a single $1s$ electron. We assume that nucleus A and electron A constitute the hydrogen atom H_A and that nucleus B and electron B make up the second hydrogen atom H_B. As the two atoms approach each other in addition to the Coulombic attraction between each nucleus and its own electron, new Coulombic attractive forces begin to operate between nucleus A and electron B, and between nucleus B and electron A. Again Coulombic repulsive forces also exist between the two electrons, and between the two nuclei.

At large distances of separation the system consists of two non-interacting hydrogen atoms. As the atoms approach each other the electrical potential energy is converted into kinetic energy. As the distance decreases, the conversion is more rapid. A critical internuclear distance is ultimately reached, at which the potential energy of the two-atom system reaches a minimum (Fig. 5.2). At this distance (0.74 A) the attractive forces balance the repulsive forces and a stable H_2 molecule results. When the internuclear distance falls below 0.74A the repulsive forces predominate and the molecule becomes unstable. A discussion on the nuclear binding forces in Chapter 12 will show that there exists a proton-proton attractive force only within the very short nuclear range of 10^{-13} cm. Below 0.74A ($1A = 10^{-8}$ cm) the forces are still electrostatic in nature and because of the proximity of the two protons the proton-proton repulsion very much out-weighs the attractive forces of one proton over the electron of the other atom. The result is dissociation of H_2 molecule into atoms.

At the optimum internuclear distance of 0.74A each nucleus exerts an attrac-

Fig. 5.2. Potential energy curve for hydrogen molecule

tive force on its own electron as also on the electron of the other atom. Consequently the two electrons forming the covalent bond are shared by the two atoms. Quantum mechanically we say that there is a very high probability of finding the pair of electrons in between the two atoms. The higher the probability the stronger is the bond, that is, the greater is the energy necessary to break the bond. In terms of orbitals of the two electrons, there occurs a significant overlap of the two $1s$ orbitals of the two hydrogen atoms, such that one electron originally confined to a single orbital can now spread itself over the other orbital (Fig. 5.3). Thus the two electrons of H_A and H_B now have a common orbital and allowing according to Pauli principle no more than two electrons per orbital, it follows that the electron spins of H_A and H_B have to be opposite if they are to share a common orbital. In the case of two hydrogen atoms with their electron spins parallel there is no minimum in the potential energy curve (Fig. 5.2) i.e. no H_2 molecule is formed. *Therefore in order that a covalent bond may be formed between two atoms a necessary condition is that each of the atoms must possess an unpaired spin.*

This general approach which emphasizes overlap of atomic orbitals of individual atoms is referred to as Valence Bond (or Atomic Orbital) method. Covalent bond formation thus can occur between two hydrogen atoms, between two fluorine atoms, and between one hydrogen atom and a fluorine atom since each fulfils the criterion of having one unpaired electron in its outer orbital. But no such molecule formation can take place between two helium atoms since helium has a configuration of $1s^2$, that is, a filled $1s$ shell with no unpaired spin.

Overlap region

H_A H_B

Covalent bond
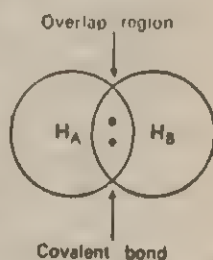
FIG. 5.3. Overlap of two $1s$ orbitals in H_2 molecule

This approach works well for very simple cases only. This simple pure atomic orbital overlap approach fails when we come to molecules like methane, boron trichloride etc. In order to cover these cases under the same overlap framework, hybridisation of pure orbitals has been invoked as a step preliminary to overlap of orbitals. Hybridisation of atomic orbitals is largely the work of Pauling and Slater.

5.2.3. Hybridisation of Atomic Orbitals. Simple valence bond theory requires the presence of unpaired electrons in an atom to enable it to participate in covalent bonding. This condition immediately limits the number of covalent bonds to the number of unpaired spins in an atom. The electronic configurations of Be, B, C are:

Be $1s^22s^2$ or $\underset{1s}{\uparrow\downarrow}$ $\underset{2s}{\uparrow\downarrow}$

B $1s^22s^22p^1$,   or $\underset{1s}{\uparrow\downarrow}$ $\underset{2s}{\uparrow\downarrow}$ $\underset{2p}{\uparrow}$ $\underset{2p}{}$ $\underset{2p}{}$

C $1s^22s^22p^2$ or $\underset{1s}{\uparrow\downarrow}$ $\underset{2s}{\uparrow\downarrow}$ $\underset{2p}{\uparrow}$ $\underset{2p}{\uparrow}$ $\underset{2p}{}$
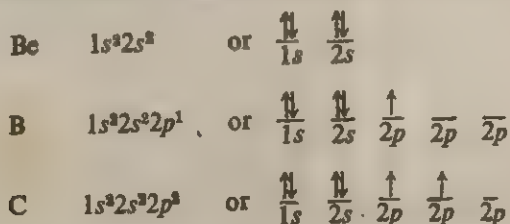
We are tempted to conclude that beryllium, boron and carbon are capable of

forming 0, 1 and 2 single covalent bonds only. Yet experimental evidences show that beryllium, boron and carbon do form 2 (in $BeCl_2$), 3 (in BCl_3) and 4 (in CH_4) covalent bonds and further that the covalent bonds of the same element are all equivalent.

In order to explain the formation of two equivalent covalent bonds by beryllium we assume that prior to reaction, one of the two 2s electrons of beryllium is promoted to the 2p level giving the excited state configuration:

$$\text{Be} \qquad \underset{1s}{\uparrow\downarrow} \quad \underset{2s}{\uparrow} \quad \underset{2p}{\uparrow}$$

Now that the excited beryllium atom has two unpaired electrons, it is capable of forming two covalent bonds by overlap with other orbitals. But as it stands, the two bonds will not be equivalent since one will involve an s bond the other a p bond. Experiments show that the bonds in $BeCl_2$ are linear and completely equivalent. Quantum mechanical calculations have shown that one s orbital and a p orbital can be mixed to generate two equivalent orbitals at 180° to each other (Fig. 5.4). These orbitals are called hybrid orbitals and carry the symbol sp to indicate their origin. (It may be added that crystalline $BeCl_2$ is polymeric and approximately tetrahedral but at ~ 750° it is monomeric and linear).

One might object to the promotion of a 2s electron to a 2p orbital as being improbable on energy considerations. However, the energy released when the excited beryllium atom forms two stable bonds with another element (say chlorine) more than compensates the energy of promotion.
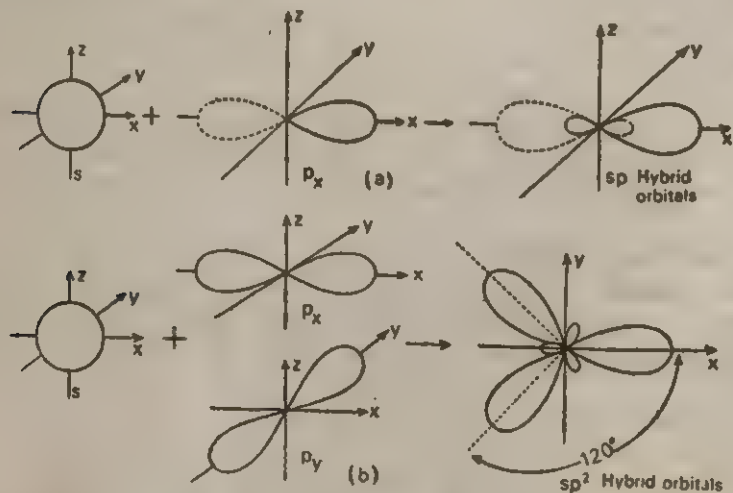
FIG. 5.4. Formation of sp and sp^2 hybrid orbitals

One 's' and one 'p' orbital give two sp hybrid orbitals in (a). Note opposite each big lobe of a hybrid orbital there is a very small lobe. This indicates that the hybrid orbitals are very directional in character and the probability of finding the electron opposite the big lobe is very low. Similar is the case for other hybrid orbitals, e.g. sp^2 hybrid orbitals in (b),

Coming to the case of boron, promotion of an electron from a 2s orbital to a 2p orbital gives the excited state configuration as:

$$B \qquad \underset{1s}{\uparrow\downarrow} \quad \underset{2s}{\uparrow} \quad \underset{2p}{\uparrow} \quad \underset{2p}{\uparrow}$$
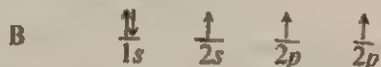
Mixing of one 2s orbital and two 2p orbitals provides three equivalent hybrid orbitals at 120° to each other. These are symbolised as sp^2 orbitals. Overlap of three such orbitals by chlorine gives the BCl_3 molecule with three equivalent bonds at 120° (Fig. 5.4). If the hybridisation scheme were not invoked then overlap of the three atomic orbitals would have resulted in three covalent bonds—two of which formed from two p orbitals, would be at 90° to each other and the third obtained from the s orbital overlap would have stayed equidistant from the other two (minimum repulsion condition), either at 135° on the same plane or at 90° in a plane at right angles to the plane of the other two bonds.

Intuitive Introduction to Hybridisation of Atomic Orbitals: Although the origin of hybridisation of atomic orbitals lies in quantum mechanical calculations it can be introduced to an honours undergraduate with a simple preassumption of the shapes of the atomic orbitals and bond angles of a given stereochemistry.

Of all the atomic orbitals only the s orbital has no directional preference i.e. it is a spherically symmetrical orbital. All the other orbitals have directional preference. For example a p_x orbital has its two lobes concentrated along the x axis. A d_{z^2} orbital has two lobes along the z axis and a ring (or doughnut) along the xy plane all around the nucleus.

I. Linear Stereochemistry: In a linear ML_2 complex the two 'L' ligands are opposite to each other i.e. the LML bond angle is 180°. Since there has to be an overlap of two orbitals of M with two orbitals of L, it follows that the two interacting orbitals of M must be disposed at 180°. No two pure atomic orbitals are known which are at 180°. Hence the concept of mixing suitable atomic orbitals of the metal ion. Let us assume that the two bonds are along the x axis. Then we can conceive of mixing the p_x orbital since it has two lobes along the x axis. Next we have to involve the only other orbital available for this purpose, namely the 's' orbital since it is spherically symmetrical. Such mixing of p_x and s will generate two hybrid orbitals which will be concentrated along the x axis. It is as if the 's' orbital is equally shared by the two halves of the p_x orbital and the resulting two hybrid orbitals will lie along x axis at 180°. In fact, two linear hybrids will be generated by mixing the 's' orbital with any of the p_x, p_y or p_z orbital.

Note also that mixing of 'n' A.O.'s generate 'n' hybrid orbitals.

II. Triangular (trigonal) Planar Stereochemistry: A complex ML_3 with a triangular planar geometry has L-M-L bond angle 120°. If we take the xy plane it follows that the three hybrid bonds equally share 360° around the metal ion in the xy plane. It follows that we have to pick up p_x and p_y orbitals as these two lie in the xy plane. With this we mix the non-directional 's' orbital. Since three atomic orbitals will yield three hybrid orbitals, these three will not only stay in the xy plane but will also encompass the 360° about the metal ion. Thus we see that the sp^2 hybrids will be at 120° to each other.

Note also that instead of taking the xy plane if we had taken the xz plane we would have to mix the 's', p_x and p_z orbitals. So sp^2 means s and any two of the three p orbitals.

III. Tetrahedral Stereochemistry: A complex ML_4 with tetrahedral geometry has L-M-L angle 109°. How do we get at it? An intuitive approach tells us that over and above ML_3 we have to raise the coordination number to four by adding one more atomic orbital to the planar sp^3. Since ML_1 is no longer planar we have to mix one such orbital which is located above and below the plane. Such an orbital is the p_z. As soon as we bring in p_z, it will force the three sp^3 hybrids so that all the four hybrid orbitals will be equivalent at the same bond angle. Thus the three planar hybrid orbitals will be pressed below the xy plane to generate a tetrahedron.

IV. Square Planar Stereochemistry: A square planar ML_4 complex has all the four bonds in the same plane with the bond angle 90°. We start from the triangular planar ML_3. To this we have to add one such atomic orbital which is also located along the same plane and whose lobes are preferably directed towards the four corners of the square plane. Assuming the xy plane as the molecular plane, we find on inspection that no p orbital can do so. But there is a 'd' orbital namely the $d_{z^2-y^2}$ orbital which has its four lobes directed along the x and y axes. Hence mixing of s, p_x, p_y and $d_{z^2-y^2}$ i.c. dsp^2 hybridisation will give us four equivalent planar hybrid orbitals.

V. Octahedral Stereochemistry: A perfect octahedron has all the six bonds equivalent and may be guessed to be formed by the mixing of two axial orbitals p_z and d_{z^2} with the square planar dsp^2. So we write it as d^2sp^3.

So the different atomic orbitals involved in the different hybrid orbitals are summarised below:

Hybridisation	Atomic orbitals
sp, sp^2	s + arbitrary p^n
sp^3	$s + p_x + p_y + p_z$
dsp^2	$dx^2-y^2 + s + p_x + p_y$
d^2sp^3	$dx^2-y^3 + d_{z^2} + p_x + p_y + p_z$

Below we summarise the common hybrid orbitals and their directional properties (Table 5.2). It should be noted that spatial arrangement fixes the shape of the resulting compounds. The usefulness of hybrid orbitals model in predicting the shapes of simple covalent molecules has been described in Chapter 6. Their utility in predicting the valence and stereochemistry of coordination complexes has been discussed in Chapter 10.

Table 5.2. Hybrid Orbitals and Directional Properties

Number of Covalent Bonds	Hybrid Orbitals	Spatial Arrangements	Examples
2	sp	linear (180°)	$HgCl_2$
3	sp^2	trigonal planar (120°)	BCl_3
4	sp^3	tetrahedral (109°)	CH_4
4	dsp^2	square planar (90°)	$K_2[PtCl_4]$
6	d^2sp^3	octahedral (90° and 180°)	SF_6

Now a final point about orbital hybridisation should be noted. Hybridisation should not be considered as a process that atoms go through. Instead hybridisation is a means of modifying the orbital overlap model to explain the formation of certain molecules. Electron waves know nothing about hybridisation. Electron waves and nuclei merely arrange themselves according to the forces that operate on them. The concept represents our mental model to explain best the results of sophisticated experiments on structure determination.

5.2.4. Valence Bond Description of Multiple Bonds. Lewis formulation of C_2H_4 molecule involves a double bond between the two carbon atoms and two single bonds each between the hydrogens and carbon. Leaving aside the question of the second bond between two carbons, each carbon assumes three equivalent planar bonds: two of these are directed to two hydrogens and the third to the other carbon. These three equivalent bonds arise out of sp^2 hybrid orbitals of carbon, and a p orbital with an unpaired electron is left out of hybridisation scheme.

$$\underset{1s}{\uparrow\downarrow} \quad \underset{2s}{\uparrow\downarrow} \quad \underset{2p}{\uparrow} \quad \underset{2p}{\uparrow} \quad \underset{2p}{} \quad \text{hybridises to} \quad \underset{1s}{\uparrow\downarrow} \quad \underset{2(sp^2)}{\uparrow} \quad \underset{2(sp^2)}{\uparrow} \quad \underset{2(sp^2)}{\uparrow} \quad \underset{2p}{\uparrow}$$
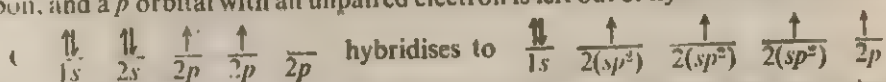
The valence bond model suggests that the overlap of the p orbitals of the two carbon atoms results in the fourth bond in C_2H_4 with the electron density concentrated in two sausage-shaped regions, one above the plane of the molecule and the other below the plane of the molecule.

The double bond area of C_2H_4 is composed therefore of two distinct parts having different electron distributions. The sp^2 hybrid orbitals overlap has symmetrical distribution of electron density about the carbon—carbon axis. *Such bond with cylindrically symmetrical distribution of electron density around bond axis is called sigma (σ) bond.* In C_2H_4 there are five sigma bonds. Bond in which the electron density is not cylindrically symmetrical around the bond axis is called a pi (π) bond. In C_2H_4 there is *one* pi bond, the electron density of which is distributed in *two* particular regions above and below the carbon—carbon axis. For a π-bond the bond axis becomes a nodal plane. A nodal plane has zero electron density. Note that the *two* sausage-shaped regions together make *one* π-bond. The pictorial representation is (Fig. 5.5):
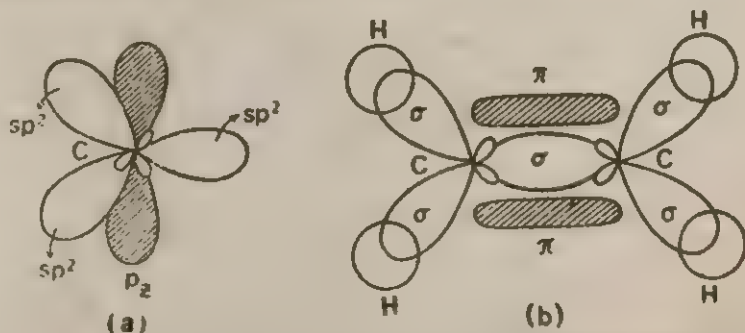
FIG. 5.5.   (a) sp^2 hybrid orbital and p_z orbital of carbon
(b) valence bond model of C_2H_4

We can extend our discussion of multiple bonding to acetylene, C_2H_2. In acetylene each carbon is sigma bonded to one hydrogen and the second carbon. To satisfy the quadrivalence of carbon there exists a triple bond between the two carbons. This triple bond is made up of one sigma bond and two pi bonds. Each carbon is sp hybridised to give a linear H–C–C–H linkage.

C $\underset{1s}{\upharpoonleft\!\downharpoonright}$ $\underset{2s}{\upharpoonleft\!\downharpoonright}$ $\underset{2p_x}{\upharpoonleft}$ $\underset{2p_y}{\upharpoonleft}$ $\underset{2p_z}{\quad}$ hybridises to $\underset{1s}{\upharpoonleft\!\downharpoonright}$ $\underset{2(sp_x)}{\upharpoonleft}$ $\underset{2(sp_x)}{\upharpoonleft}$ $\underset{p_y}{\upharpoonleft}$ $\underset{p_z}{\upharpoonleft}$

One sp_x electron forms a sigma overlap with the $1s$ electron of hydrogen and the second sp_x electron makes the second sigma overlap with another sp_x electron of the second carbon. The two $2p_y$ orbitals overlap to give one pi bond. Similar overlap of the $2p_z$ orbitals of the two carbons makes the second pi bond. Thus acetylene is a linear molecule made up of three sigma bonds and two pi bonds.

We have seen earlier (4.5) that bond length decreases with increasing multiplicity of a bond. We can now state that *addition of one (or two) π-bond (s) to a σ bond decreases the bond length.*

Distinctions between sigma and pi bonds: 1. Because of a head-on overlap along the bond axis the sigma bond is stronger than a pi bond where the overlap is sideways and not along the bond axis. Note the energy of a C–C sigma bond is 83 KCal/mole while that of a C–C pi bond is 63 KCal/mole

2. The electrons of the weaker pi bond are more spread out in space and are therefore more exposed to any chemical reagent.

3. Due to cylindrical symmetry free rotation of atoms about a sigma bond is allowed. Similar rotation about a pi bond will lead to decrease in overlap because coplanarity of the pi orbitals overlap will be destroyed and hence rotation about a double or triple bond is hindered.

4. A sigma bond is cylindrically symmetrical about the bond axis but a pi bond is not so.

5. A sigma bond determines the direction between the bonding atoms but a pi bond has no primary effect in this respect.

5.2.5. Resonance. While presenting a simplified picture of the valence bond model of the hydrogen molecule we have referred to the interaction of one nucleus on its own electron as well as on the electron of the other hydrogen atom. Because of this and because of our inability to distinguish between the electrons of the two hydrogen atoms, four electronic structures may be written to describe the H_2 molecule:

$$H_A^{\cdot A}\!\!-\!\!^{B\cdot}H_B; \quad H_A^{\cdot B}\!\!-\!\!^{A\cdot}H_B; \quad H_A^{\cdot\cdot} \quad H_B^{+}; \quad H_A^{+} \quad :H_B^{-}$$
$$\quad\;\; I \qquad\qquad\quad II \qquad\qquad III \qquad\quad IV$$
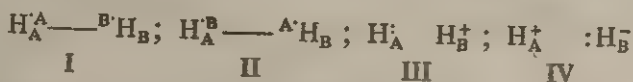
Although we write four structures for the H_2 molecule, none of these structures adequately describes the molecule. The molecule does not possess any of the four structures any time in its ground state life. The actual structure is considered as an intermediate, that is, a resonance hybrid of all the above four structures. All

the resonating structures (canonical forms) are assumed to contribute to the actual structure, the contribution depending on the particular structure. Of the above four structures it can be guessed that structures I and II will make equal and much greater contribution to the resonance hybrid than structures III and IV. Because of high ionisation potential of hydrogen the ionic structures III and IV make little contribution.

Recalling the octet rule the following structures can be written for SO_2.
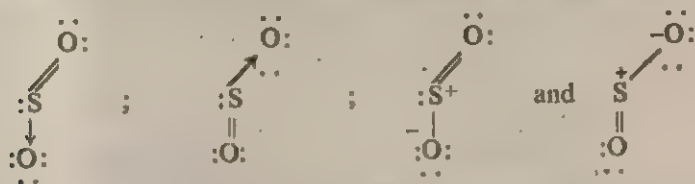
Anyone structure implies that there are two different kinds of bonds in the SO_2 molecule. We would expect that the oxygen attached by a double bond would be closer to the sulphur atom than the single bonded oxygen. Experiments show that both the sulphur-oxygen bond lengths are the same (1.43A) and is intermediate between a single bond and a double bond. The actual structure obtaining in SO_2 molecule is a resonance hybrid of the above structures. Other common examples where resonance structures can be written are SO_3, NO_3^-, benzene etc.

The following points may be noted on resonance:

1. Resonance forms (structures) do not imply different kinds of molecules.

2. Resonance forms are anticipated when a molecule can be represented by two or more Lewis structures.

3. In writing resonance forms the relative positions of the atoms must remain the same. For example, a structure $: S \rightarrow \overset{..}{O} = \overset{..}{O} :$ cannot be a resonance form of SO_2 molecule. If we change the positions of the atoms we are not writing the structure of the same compound but doing so for an isomeric species.

4. Resonance forms must have the same number of unpaired electrons.

5. The actual structure (resonance hybrid) is more stable than any of the resonance forms. The amount of energy by which the actual structure lies below the more stable of the resonance form is called the resonance energy. Assuming that we have a system which can be represented by two structures of wave functions Ψ_I and Ψ_{II} we can write a Ψ for the actual system such that $\Psi = a\Psi_I + b\Psi_{II}$, a and b being arbitrary numerical coefficients. A value of b/a may be chosen such that the energy of the system becomes minimum—a value which will be lower than the lower of the two structures. This lowering of energy is the *resonance energy*. Appendix III provides the necessary quantum mechanical background.

6. Resonance forms possess similar energies.

7. All the resonance forms do not contribute equally to the actual structure. For example, of the following three structures of HCl molecule,

$$H : \overset{..}{\underset{..}{Cl}} : \quad ; \quad H^+ \quad : \overset{..}{\underset{..}{Cl}} : \quad ; \quad H :^- \quad \overset{..}{\underset{..}{Cl}} :^+$$
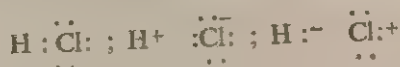
the contribution of the last one to the actual structure must be poor since chlorine is much more electronegative than hydrogen and is unlikely to be positive.

8. Resonance forms differ only in the distribution of the electrons among the bonding atoms.

Distinctions between resonance forms and tautomers: Tautomers are two distinct i.e. different chemical species with the same empirical composition, which are in dynamic equilibrium. In tautomers there is no restriction with the relative positions of the atoms i.e. atom positions are different. But in the resonance forms the position of the atoms are fixed and no equilibrium is involved. The commonest example of tautomers is keto-enol tautomers:

$$
\begin{array}{ccc}
\underset{\text{(keto)}}{\begin{array}{c} CH_3 \\ H_3C-C=O \\ H_3C-C=O \end{array}}
& \rightleftharpoons &
\underset{\text{(enol)}}{\begin{array}{c} CH_3 \\ HC=C-OH \\ H_3C-C=O \end{array}}
\end{array}
$$
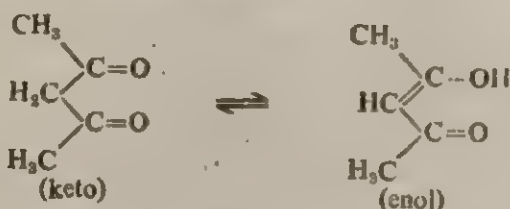
5.2.6. Molecular Orbital (MO) Theory of Covalent Bond.

The valence-bond model of the covalent bonding accounts for the stability of a molecule in terms of overlap of atomic orbitals. With the introduction of hybridisation concept the theory can take care of the number of bonds formed by atoms and also of the angles between these bonds. Further, if we accommodate the concept of resonance, valence bond theory is capable of explaining the structures of molecules such as SO_2 for which more than one Lewis structure can be written.

Unfortunately the valence bond theory has its weak points too. For example, diatomic molecular oxygen can be represented by the formula:

$$:\overset{..}{O} = \overset{..}{O}:$$

The structure involves an overlap of two p orbitals of the two oxygen atoms to form a σ bond and an overlap of two other p orbitals to form a π bond. It turns out that according to this formula the molecule has no unpaired electron. Experiments have, however, indicated that molecular oxygen is paramagnetic to the extent of two unpaired electrons. Valence bond theory also predicts that the B_2 molecule, with the structure $:B-B:$ should have no unpaired electron. Magnetic studies show that the molecule has two unpaired electrons.

The deficiencies of the valence bond theory are due to an oversimplification inherent in its approach. It assumes that electrons in a molecule can be found in atomic orbitals of the individual atoms. For example in methane, CH_4. a pair of bonding electrons are most likely to be found in between two nuclei (overlap region of sp^3 orbital of carbon and $1s$ orbital of hydrogen) but there is also a finite probability of finding the pair on $1s$ orbital of hydrogen or on the sp^3 orbital of carbon alone. The VB picture is clearly an approximation. It appears more satisfactory to locate these electrons in molecular orbitals, orbitals which are character-istic of the molecule as a whole. In the derivation of electronic structure by this

method all the electrons are considered to belong to the molecule. Just as we introduce atomic electrons into atomic orbitals, molecular electrons go to molecular orbitals. The molecular orbital theory is largely the work of Mulliken. The necessary quantum mechanical treatment of the M.O. theory appears in Appendix II.

Several important features of the molecular orbital approach are enumerated below:

1 Atomic orbitals of the individual atoms can be combined to give rise to molecular orbitals. The number of molecular orbitals formed is equal to the number of atomic orbitals involved in the combination. In order that fruitful molecular orbitals can result, the energies of the atomic orbitals of the combining atoms must be close to each other. In case the atomic orbitals differ widely in their energies, then calculations show that the energies of the molecular orbitals become the energies of the starting atomic orbitals, that is, no effective combination of atomic orbitals takes place.

2. Two atomic orbitals produce two molecular orbitals, one of which has an energy lower than that of the lower energy atomic orbital and the other has an energy higher than the higher energy atomic orbital. The lower energy molecular orbital is called a bonding orbital and the higher energy orbital is called an anti-bonding orbital (Fig. 5.6). It will be observed (Fig. 5.6) that the bonding orbital has a high electron density in the region between the two nuclei, accounting for the stability. In an antibonding orbital the probability of finding an electron in
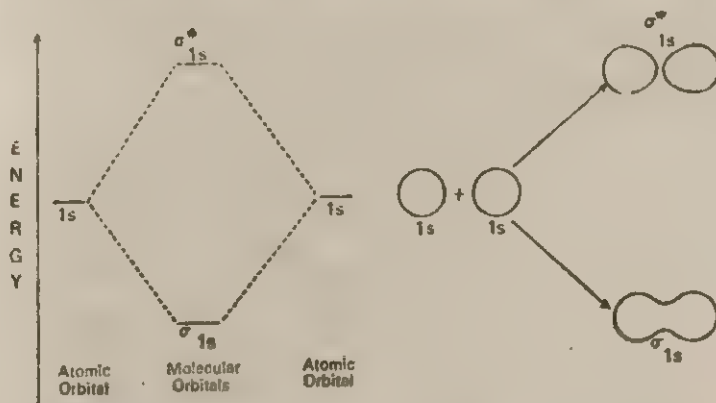
FIG. 5.6. Molecular orbitals formed by combining two 1s orbitals

between the nuclei is very small; the electron density is concentrated at the far ends of the molecule. Since the nuclei are now less shielded from each other (because of no electron density in between them) than they are in isolated atoms, the antibonding orbital is unstable with respect to the starting atomic orbitals. Since the electrons prefer to keep away from the bonding area the nuclei tend to repel. The electron density in both these bonding and antibonding orbitals is symmetrical with respect to the bond axis and therefore both are sigma (σ) molecular orbitals.

Extension of these ideas to π type atomic orbitals would give bonding π molecular orbitals and antibonding π^* molecular orbitals If x direction is taken as the bond axis then combination of two p_x orbitals would give one bonding and one anti-
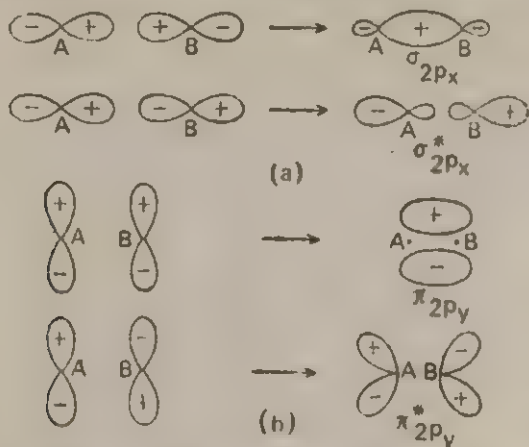
Fio. 5.7. Molecular orbitals formed from σ and π type p orbitals

bonding σ molecular orbital. Combination of two p_y orbitals, and of two p_z orbitals can provide two π molecular orbitals each (Fig. 5.7).

3. Inner orbital electrons of the individual atoms do not participate in the formation of molecular orbitals. Therefore the individual atomic nuclei along with their inner shell electrons are placed in proper bonding distance (for H_2 at 0.74A), and then the remaining electrons are placed in the molecular orbitals.

4. The sign ($+$ or $-$) of the wave function of the combining atomic orbitals is very important. When the overlapping lobes of the combining atomic orbitals have the same sign we get a bonding molecular orbital. dissimilar sign produces an antibonding orbital. In Fig. 5.7(a) the two p_x ($p\sigma$ type) orbitals with '+' sign on the overlapping lobes produces the bonding σ_{2p} molecular orbital. When the two lobes face each other with opposite sign we get the σ^*_{2p} antibonding molecular orbital. In 5.7(b) the two p_y ($p\pi$ type) orbitals with '+' sign on both the upper lobes and '$-$' sign on both the lower lobes we have a good bonding π_{2p} molecular orbital. With dissimilar sign the antibonding π^*_{2p} orbital is produced.

5. Valence (that is, outer orbital) electrons are distributed among the molecular orbitals the same very way as atomic electrons in atomic orbitals. Explicitly we find:

(a) each molecular orbital can accommodate a maximum of two electrons

(b) electrons occupy lowest energy molecular orbital. Higher energy orbitals will not be filled as long as low energy levels are available.

(c) when two equal energy molecular orbitals are available electrons will tend to remain unpaired so long as they can avoid pairing.

We can now proceed to examine a few simple molecules. The two $1s$ orbitals of two hydrogen atoms combine to give two molecular orbitals, σ_{1s} and $\sigma_1^*_s$.

Since the energy gap between the two molecular orbitals is big enough both the electrons remain paired in σ_{1s} molecular orbital. Taking the example of O_2 molecule we have to accommodate a total of twelve electrons in the molecular orbitals. From the diagram (Fig. 5.8) there will be two electrons in each of the molecular orbitals σ_{2s}, σ_{2s}^*, σ_{2px}, π_{2py} and π_{2pz}. The next higher energy orbitals are π^*_{2py} and π^*_{2pz} and both are of equal energy. Hence the eleventh and twelfth electron need not pair them. They will remain unpaired one each in π^*_{2py} and
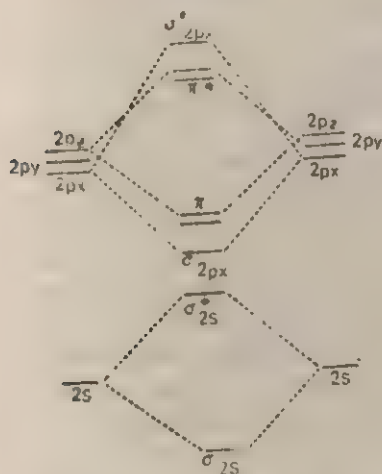
Fig. 5.8. Molecular orbital diagram from 2s and 2p atomic orbitals
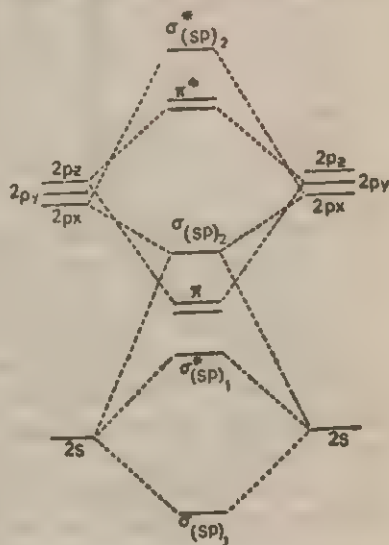
Fig. 5.9. Molecular orbital diagram allowing s—p interaction

π^*_{2pz} orbitals. Therefore the molecule will show paramagnetism corresponding to two unpaired electrons. The diagram in Fig. 5.8 is however over simplified. It assumes that there is no interaction between the 2s orbital and the $2p_x$ orbital. Since we assume x direction as the bond axis the symmetry of the molecule will permit some interaction between the 2s and $2p_x$ orbitals, although they are somewhat different in energy. Allowing for the s-p interaction a second diagram (Fig. 5.9) can be drawn. Some common and simple diatomic molecules are included in Table 5.3 and the electron distribution in their molecular oribtals is examined according to Fig. 5.9. The reader may check that had we relied on the simpler diagram of Fig. 5.8, the B_2 molecule would have shown no unpaired electrons. But experiments show that the molecule carries two unpaired electrons.

In the molecular orbital model it appears to be a somewhat difficult proposition to keep track of the number of bonds formed. It is convenient to consider that a full bond between any two atoms is made up of two electrons. Thus we define as a theoretical quantity the number of bonds (bond order) in a molecule thus;

$$\text{number of bonds (bond order)} = \frac{\text{(number of electrons in bonding MO's)} - \text{(number of electrons in antibonding MO's)}}{2}$$

Table 5.3. Electron Distribution in Molecular Orbitals of some Simple Molecules according to Fig. 5.9.

Molecule	$\sigma(sp)_1$	$\sigma^*(sp)_1$	$\pi(2p)$		$\sigma(sp)_2$	$\pi^*(2p)$		$\sigma^*(sp)_2$	unpaired electrons
B₂	↑↓	↑↓	↑	↑					2
C₂	↑↓	↑↓	↑↓	↑↓					0
N₂	↑↓	↑↓	↑↓	↑↓	↑↓				0
O₂	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑		2
F₂	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓		0
CO	↑↓	↑↓	↑↓	↑↓	↑↓				0
NO	↑↓	↑↓	↑↓	↑↓	↑↓	↑			1

Effectively one electron in an antibonding MO is assumed to cancel out the bonding stability induced by an electron in a bonding MO. Using this definition we find in H_2 we have one σ bond, in O_2 one σ and one π, in N_2 one σ and two π bonds.

With reference to Fig. 5.8 and Table 5.3 we note that bond order (i.e. bond multiplicity) of O_2 is 2 while that of O_2^+ is 2.5. Again bond order of N_2 is 3 but that of N_2^+ is 2.5. Since bond dissociation energy (section 5.2.11) decreases with decreasing bond order we can safely predict that bond dissociation energy of O_2^+ will be greater than that of O_2 while the bond dissociation energy of N_2 will be larger compared to that of N_2^+. The relative bond dissociation energies of NO and N_2 are left to the reader as exercise.

5.2.7. Properties associated with Covalent Bond

1. Covalent crystal lattices are built up of molecules, instead of ions. Isolated, discrete molecules are held together by weak van der Waals forces.

2. Covalent bonds are directional in nature. Consequently a close packed type system in the sense of ionic compounds cannot be formed. Covalent crystals have open structures as opposed to close packed type structures of ionic compounds.

3. Since covalent molecules are held together by weak intermolecular forces the crystal lattice can be more easily ruptured. They are soft and have low melting and boiling points.

4. Since covalent molecules are not made up of ions, they cannot be dragged into polar solvents by ion-dipole interaction. However in special cases solubility of covalent compounds in polar solvents may be facilitated through the agency of hydrogen bonding.

In discussing solubility of covalent compounds organic chemists talk of a rule: *like dissolves like*. The intermolecular forces that hold together the molecules of a covalent solvent and the molecules of a covalent solute are similar (of van der Waals type). Hence it is quite possible that the similar intermolecular forces will be able to bind solute molecules to solvent molecules. Therefore a non-polar covalent compound is likely to dissolve in non-polar organic solvents.

For example methane will dissolve in carbon tetrachloride. Further, highly polar methanol is quite soluble in polar water. This time dipole-dipole interaction between H_2O molecules, and between CH_3OH molecules are similar. Dipole-dipole interaction can now operate between H_2O and CH_3OH molecules and hence the solubility of methanol in water.

5. Covalent compounds are non-conductors.

6. The reactions of covalent compounds in solution are characteristic of the whole molecule or of constitutional functional groups. These reactions involve rupture and formation of covalent bonds and hence are slow and have measurable rate.

It is interesting to note that the detection of covalently bonded elements (N. S, halogens) in organic qualitative analysis cannot be done unless these elements are converted into ionic forms for which we have characteristic ionic reactions known. For this reason all organic compounds are decomposed by sodium fusion and converted to sodium salts of characteristic anions.

The above properties are but of pure covalent compounds. Exceptional behaviour will always arise in exceptional cases. Diamond, for example, is a covalent substance made of non-ending tetrahedral sp^3 bonding between carbons themselves. Since a 'giant' 'molecule' is present all through the crystal lattice the substance sublimes at a high temperature ($\sim 3500°C$). Silicon carbide, silicon dioxide also have comparable properties. The structure of graphite (see Part II) shows a covalent layer structure but with mobile π electrons which gives it conducting properties.

5.2.8. Deformation of Ions—Passage from Ionic to Covalent Bonding (Fajans' rules). Coulombic attraction between cations and anions in ionic compounds may in certain cases lead to considerable deformation of the ions. Distortion of electron distribution in a molecule or ion caused by another molecule or ion is known as *polarisation*. This deformation (polarisation) of ions may give rise to an appreciable increase of electron density in between the two nuclei—a situation leading to covalent bonding (Fig. 5.10). The charge and size of the cation and of the anion are responsible for such passage of an ionic bond to a covalent bond. The following rules are useful:

1. The more highly charged a cation is the more effective it is in polarising the anion. Polarising power of a cation is dependent on its charge/radius ratio and is greatest for small, highly charged cations. Polarising power varies as: $B^{3+} > Be^{2+} > Li^+$.

2. The more highly charged an anion is the more difficult it is to control the outer orbital electrons. It is therefore easily polarised.

FIG. 5.10
Polarisation of ions

3. The smaller the size of the cation the more efficient it is in polarising the anion: $Li^+ > Na^+ > K^+$.

4. The larger the size of the anion the more difficult it is to control the outer electrons. A large anion is therfore easily polarised: $I^- > Br^- > Cl^- > F^-$.

5. Given the same charge and similar size a pseudo noble gas type cation (18 electron shell as in Cu^+, Ag^+ etc.) will be more easily deformed than a cation of noble gas type. This is due to the poor shielding ability of the d electrons of the pseudo noble gas cation. As a consequence such cations are easily polarised by the anions. However this polarising effect is to be regarded as of minor significance compared to other sources of polarisation listed above.

These rules are known as Fajans' rules and are good guides for predicting the types of compound to expect. We now discuss how well these rules stand out. The melting points and boiling points of some compounds are given in Table 5.4 and Table 5.5. Melting points are indicative of the thermal energies required to separate oppositely charged ions (in the case of an ionic compound) or molecules (in the case of covalent compounds) so as to give to the compound the freedom of motion characteristic of the liquid state.

Table 5.4. Melting Point (°C) and Boiling Point (°C) of some Compounds

Compound	M.P.	B.P.	Compound	M.P.	B.P.
NaF	988	1695	CF_4	−183.7	−129
NaCl	801	1413	CCl_4	−22.9	76.7
NaBr	755	1390	CBr_4	90	190
NaI	651	1304	CI_4	171 decomp.	—

Table 5.5. Effect of Ionic Size and Charge on Melting Point (°C)

Compound	Charges on the ions	$r^+ + r^-$ (A)	M.P.
NaF	+1, −1	0.95 + 1.36 = 2.31	988
NaCl	+1, −1	0.95 + 1.81 = 2.76	801
NaBr	+1, −1	0.95 + 1.95 = 2.90	755
NaI	+1, −1	0.95 + 2.16 = 3.11	651
MgO	+2, −2	0.65 + 1.40 = 2.05	2800
CaO	+2, −2	0.99 + 1.40 = 2.39	2570
BaO	+2, −2	1.35 + 1.40 = 2.75	1920

Note that with carbon in +4 oxidation state, the charge on the hypothetical cation is prohibitively large and as a consequence low melting and low boiling covalent compounds are formed (Table 5.4).

Small charge and large size for a cation, and small charge and a small size of an anion are the best guarantee for an ionic compound. The variation in respect of melting points of ionic compounds is understandable from Coulomb's law. The attractive force between oppositely charged ions is given by:

$$F \propto \frac{q_1 q_2}{(r^+ + r^-)^2}$$

where q_1 and q_2 are the charges on the ions and r^+ and r^- are ionic radii of the cation and the anion respectively. Given the same charge on the ions if the sum of the ionic radii increases the force between them will decrease and the compound will register a lower melting point. This is exemplified by the series NaF to NaI. On the other hand if the sum of the radii remains the same but the charge increases then force will increase and hence also the melting point. This is nicely shown by NaCl and BaO; by NaF and CaO (Table 5.5).

The interionic forces are expected to be the largest for small ions of high charge. These extreme forces really lead to deformation of ions and an ionic compound passes on to a covalent molecule.

For predominantly covalent compounds the melting points and boiling points are roughly functions of their molecular weights. This is demonstrated by the data in Table 5.4 for the halides of carbon.

A change in the type of bonding is often detectable from a scrutiny of the melting points or boiling points. In Table 5.6 SnF_4 sublimes at 705°C which is far larger than the melting points of $SnCl_4$, $SnBr_4$ and SnI_4. For the last three melting points increase with molecular weight (characteristic of covalence). Thus SnF_4 is to be regarded as an ionic compound, the other three being covalent. Aluminium halides also show a comparable trend (Table 5.6).

Table 5.6. Melting Points (°C) of AlX_3 and SnX_4

Compound	Melting Point (°C)	Compound	Melting Point (°C)
AlF_3	1291 sublimes	SnF_4	705 sublimes
$AlCl_3$	177.8 ,,	$SnCl_4$	−33
$AlBr_3$	97.5 ,,	$SnBr_4$	31
AlI_3	191 ,,	SnI_4	144.5

The higher the oxidation state of the cation the more is the covalent character. Compounds in lower oxidation states will be more ionic. This is exemplified by the melting points and boiling points of tin (+ 2 and + 4), lead (+ 2 and +4) and thallium (+ 1 and + 3) (Table 5.7). *In general, low oxidation states of metals are metallic and high oxidation states often have non-metallic properties.*

Table 5.7. Variation in Melting Point and Boiling Point with Oxidation States

Compound	M.P. (°C)	B.P. (°C)	Compound	M.P. (°C)	B.P. (°C)
$SnCl_2$	246	652	TlCl	430	720
$SnCl_4$	−33	114			
$PbCl_2$	501	950	$TlCl_3$	25	decomposes
$PbCl_4$	−15	105 explodes			

The effectiveness in forcing covalent character by a pseudo noble gas type cation as compared to that of a noble gas cation is shown by the data in Table 5.8.

Note also that although the melting points indicate what we expect, the boiling points do not lend unequivocal support.

Table 5.8. Melting Points and Boiling Points of Chlorides of some pseudo Noble gas type Cations.

Compound	Cation Radius (A)	M.P. (°C)	B.P. (°C)
NaCl	0.95	801	1413
CuCl	0.96	422	1366
KCl	1.33	776	1500
AgCl	1.26	455	1550
CaCl$_2$	0.99	772	1600
CdCl$_2$	0.97	568	964

5.2.9. Deformation of ions: Diagonal relationship in the Periodic Table. Connected with the deformation of ions is what is called diagonal relationship in the Periodic Table. In the first two short periods we have three pairs of elements which show close similarity in their chemistry although they are members of different groups. These pairs are Li, Mg; Be, Al; and B, Si. We can reach magnesium from

Li   Be   B   C

Na   Mg   Al   Si
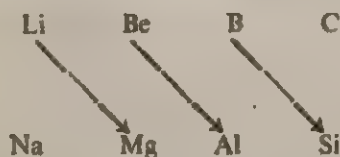
lithium in either of two routes. A movement from lithium to beryllium raises the charge on the cation and further decreases the size of the cation. This helps in attaining a good degree of covalence in beryllium. But moving from beryllium to magnesium in the same group increases the size of the cation, charge remaining the same. Thus ionic bond is favoured. The overall effect of moving from lithium to magnesium is to arrive at an ion of similar deforming power. We get to the same conclusion if we first move from lithium to sodium and then to magnesium. Such diagonal relationship does not extend to other periods since with further increase in atomic number the size and charge vary rather less drastically and are not as much effective in polarising the ions as they are in the first two short periods.

From the preceding section we have seen that interionic forces will be large when q_1/r^1 and q_2/r^2, that is, *charge/radius ratio* (*ionic potential*) is large. For pairs of elements showing diagonal relation it is expected that their charge/radius ratios should be close enough to lead to similar properties. The following data provide some clue (Table 5.9).

Table 5.9. Charge/Radius ratios of Diagonal pairs

	Li	Mg	Be	Al	B	Si
Charge	+ 1	+ 2	+ 2	+ 3	+3	+ 4
Radius of the ion (A)	0.60	0.65	0.31	0.51	0.2	0.39
Charge/radius (ionic potential)	1.6	3.08	6.4	6.0	15	10.3

However charge/radius ratio may not rescue us always. For instance charge/radius ratio of sodium is 1.05 so that lithium must have more resemblances with sodium than with magnesium.

5.2.10. Ionic Potential and its Usefulness. The charge by radius ratio of a metal ion is called its ionic potential. As the charge by radius ratio gets large we witness a large charge associated with a small ionic radius. A cation with a large ionic potential will be more electronegative and this property helps us to draw some general conclusions about variation of properties with changing ionic potential.

1. If two elements are diagonally related and have close ionic potential then they will give rise to so-called diagonal relationship (see earlier section).

2. The larger the value of the ionic potential the greater is the tendency towards covalence and complex formation. This is what has been predicted by Fajans.

3. Electronegativity increases with ionic potential. Hence the oxides of metal ions with higher ionic potential are likely to be acidic rather than basic. With increasing electronegativity the metal ion forms strong covalent bond with oxygen and hence in water such oxides liberate H^+ ions rather than OH^- ion. (cf: 8.12.3)

4. Carbonates of those metals with high ionic potential readily decompose on heating. This is due to the fact that the highly electronegative element tends to drag an oxygen of the carbonate ion forming metal oxide and releasing carbon dioxide.

5. Solvation or hydration energy is defined as the energy released when one gram ion of a metal ion in the gaseous state reacts with a given solvent or water to produce solvated or hydrated ion. It is easily guessed that an ion with high value of ionic potential will tend to form a solvo- or aquo complex more readily than an ion with a smaller ionic potential. In other words solvation or hydration energy increases with increasing potential.

5.2.11. Bond multiplicity, Bond Length and Bond Dissociation Energy :

1. *As bond multiplicity (i.e., bond order) increases bond length decreases.*
2. *As bond multiplicity increases bond dissociation energy increases.* For supporting data see section 4.5.
3. *Bond length depends also on the nature of hybridisation.*

Hybridisation and orbital size: Size of a hybrid orbital is dependent on the type of hybridisation. An *s* orbital extends less in space about the nucleus com-

pared to a p orbital. Therefore the size of hybrid orbitals will increase in the order: $sp < sp^2 < sp^3$ because of increased participation of bigger sized p orbitals. Thus C-H bond length in the hydrocarbon ethane (sp^3), ethylene (sp^2) and acetylene (sp) are 1.112A, 1.103A and 1.08A respectively. Note that in sp, sp^2 and sp^3 hybrid orbitals the s and p characters are 50%, 50%; 33%, 66%; and 25%, 75% respectively.

    4. *Bond length is also influenced by resonance :*

In the sulphate ion (see Part II) all the four sulphur-oxygen bonds become equivalent through resonance and have the same bond length 1.44A.

5.3. THE METALLIC BOND

The metals constitute about three-fourths of the elements in the Periodic Table. It appears that elements with too little electrons in the outer shell but with too many orbitals behave as metals. Before we proceed to discuss the type of bonding in metals it is only wise to look into their special properties.

High Electrical Conductivity: The metallic elements have electrical conductivity, which is many thousand times greater than those possessed by non-metals. The high conductivity implies the presence of large number of mobile electrons which can move under the influence of an electric field.

High Thermal Conductivity: Among solid substances, metals are by far the best conductors of heat. Our cooking utensils bear testimony to this property of metals.

Lustre: Polished metal surfaces are good reflectors of light, and hence the surface appears shiny.

Emission of Electrons: Metals release electrons when they are heated sufficiently (thermionic emission) or when they are exposed to light of proper frequency (photoelectric effect). This property again indicates the presence of mobile electrons in metals.

Formation of Cations: When reacting with non-metallic elements, metals are known to give cations, once again indicating that electrons are readily separated from the metallic lattice.

Since all the atoms in a metal are alike it is most unlikely that one atom would release its valence electron to another similar atom. Simple localised covalent bonding by electron sharing between two metal atoms also cannot give an octet or noble gas structure. A valence bond picture with inclusion of resonance concept, and a molecular orbital approach have provided satisfactory explanations of many of the metallic properties.

    5.3.1. The Electron-Sea Model of the Metallic Bond. Crystal lattice of lithium metal consists of an arrangement of lithium atoms at the points of a body centred cubic lattice. Each lithium atom has as nearest neighbours eight other lithium atoms. Lithium-lithium distance is 3.04 A. The atomic radius of lithium being 1.52 A, this distance indicates an electron-pair bond between two lithium atoms. Again quantum mechanical calculations give 3.02 A as the lithium-

lithium one-electron bond distance. Therefore lithium crystal may be pictured as involving both two-electron bond and one-electron bond. These bonds are not fixed, however, but resonate among the various pairs of atoms.

The above picture of metallic bond implies that the bonding electrons are not tied to any particular pair of metal atoms, as is the case in usual electron-pair covalent bond, but are spread out over a wide region. This concept is called the electron-sea model of the metallic bonding. Metallic lattice is thus composed of a regular pattern of positive metal ions (Li^+, Cs^+, Ba^{2+} etc.) firmly positioned in a sea of mobile electrons. The valence electrons can move about freely in the crystal lattice.

This model can explain most of the metallic properties. Under the influence of an applied electric field it is possible for these loosely bound electrons to move through the lattice thereby conducting a current. Heat conduction is also a consequence of the freedom of motion of electrons. A higher temperature at one point means that the atomic cores at that point have higher kinetic energy than those at other points. The higher energy atomic cores transfer some energy to the mobile electrons, which in their turn transfer the energy to atomic cores at other distant points. Since the mobile electrons are not tied to a particular bond with a characteristic energy, they can absorb and reemit light of all wave lengths. A metal thus becomes a good reflector and we find an explanation of its lustre. In a metal crystal lattice, an atom is not greatly restricted in regard to the number and directions of the bonds it can form with its neighbouring atoms. As a consequence, even if the metal is deformed, it is capable of forming bonds as strong as the original ones. The metal structure thus permits healing, and we say a metal is malleable and ductile. Electron emission properties have a ready explanation in the mobile, loosely bound electrons escaping from the metallic lattice on application of sufficient heat or light.

Although the electron-sea model qualitatively explains so many properties of metals, it stumbles on the question of molar heat capacity of metals. It is difficult to explain why the molar heat capacity of metals is not considerably higher than that of non-metals. The mobile electrons are expected to make a significant contribution to the heat capacity.

5.3.2. The Band Theory of Metallic Bond. This theory is an extension of the molecular orbital theory to metallic structure. We recall that n atomic orbitals can be combined to give n molecular orbitals (Fig. 5.11), of which one-half will be of the bonding type and the other half will be of the anti-bonding type. In a metallic crystal n may be considered to be 6×10^{23} (Avogadro number) so that there are 3×10^{23} bonding and 3×10^{23} antibonding molecular orbitals. Since the starting atomic orbitals are of similar energy (in lithium it is the $2s$ orbital) the bonding and also the antibonding molecular orbitals give rise to a *band consisting of a very large number of very closely spaced molecular orbitals.* Remembering that each molecular orbital can accommodate only two electrons, it is expected that the lower half of the levels, that is, bonding molecular orbitals will be occupied

by electrons. The other half, that is, antibonding orbitals will remain unfilled (Fig. 5.11).
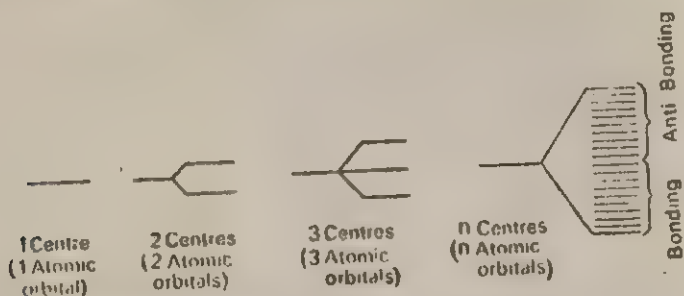
FIG. 5.11. Band formation of metal orbitals

When a crystal of lithium is placed in an electric field, a few electrons acquire enough energy to move into the higher unoccupied antibonding orbitals. These high energy electrons carry the current. The high conductivity of metals is thus attributable to the large number of antibonding molecular orbitals which differ slightly in energy from the electron-occupied bonding orbitals. The high energy electrons can also explain the other metallic properties. In addition this model explains why the electrons in a metal under ordinary conditions make only a small contribution to the heat capacity. When the temperature is raised the overwhelming majority of the electrons still remain in their original bonding molecular orbital and so absorb no heat.

5.4. POLARITY OF MOLECULES

A polar molecule is one in which there is a separation of the centres of gravity of the positive and negative charges. The molecule develops a positive and a negative pole. In an electric field the dipolar molecules tend to align themselves such that the positive ends face the negative pole of the electric field and the negative ends face the positive pole. The polarity of a molecule is quantitatively expressed as its dipole moment. *Dipole moment is defined as the product of the charge* (δ) *and the distance* (d) *of separation of the charges* (i.e. $\mu = \delta \times d$). Perfectly non-polar compounds register zero dipole moment and the polar ones positive values (Table 5.10). Since the charge is usually of the order of the charge on the electron $(4.8 \times 10^{-10}$ esu), while the distance of charge separation is of the order of angstrom, a convenient measure of the dipole moment is in 10^{-10} esu A or 10^{-18} esu cm units, called the Debye unit (D).

A binary homonuclear molecule has to be nonpolar since the bonding elements possess same electronegativity. Heteronuclear diatomics, as a rule, are polar due to a difference in their electronegativity. However electronegativity difference is not the only criterion of polarity. Polarity is also decided by the composition and geometry of the molecule. Thus the linear BeF_2 has widely differing electronegativities in beryllium and fluorine. The fluorine ends have some residual negative

Table 5.10. Dipole Moments (per molecule) of some common Compounds

Compound	Dipole moment (D)	Compound	Dipole moment (D)
H_2	0	H_2O	1.84
Cl_2	0	H_2S	0.92
CH_4	0	NF_3	0.20
BCl_3	0	NH_3	1.46
HF	2.00	CCl_4	0
HCl	1.03	$CHCl_3$	1.15
HBr	0.79	CH_2Cl_2	1.59
HI	0.38	CH_3Cl	1.86

1 Debye (= D) = 10^{-18} esu cm = 10^{-10} esu A
A molecule wherein the unit positive and negative charges are separated by 0.21 A
has 'a dipole moment of one Debye. (In SI unit 1 D = 3.33×10^{-30} coulomb
metre)

---

charge and the beryllium has residual positive charge ($F\delta^- - Be\delta^{++} - F\delta^-$). The
centres of gravity of the positive and negative charge coincide on beryllium. When
we come to H_2O the molecule is no longer linear but has H—O—H angle of 104°.
The molecule may be viewed to be formed by the overlap of *two sp³* hybrid orbitals
of oxygen (with an unpaired spin on each)

$$O \quad \underset{2s}{\uparrow\downarrow} \; \underset{2p}{\uparrow\downarrow} \; \underset{2p}{\uparrow} \; \underset{2p}{\uparrow} \quad \text{hybridises to} \quad \underset{2(sp^3)}{\uparrow\downarrow} \; \underset{2(sp^3)}{\uparrow\downarrow} \; \underset{2(sp^3)}{\uparrow} \; \underset{2(sp^3)}{\uparrow}$$
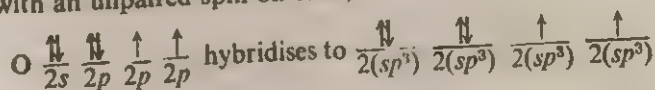
with two 1s orbitals of two hydrogens. There will be two lone pairs on the remain-
ing sp³ hybrid orbitals of oxygen. Owing to the greater electronegativity of oxygen
the electrons of the H—O bonds spend more time around oxygen than around
hydrogens. The dipole moment of H_2O arises from two contributions: (a) from the
electronegativity difference of H and O i.e. from the bond polarity and (b) from
the lone pairs (Fig. 5.12). The sign $\overset{+}{\longrightarrow}$ indicates the direction of shift of
electron density.

A comparison of the magnitude
of the dipole moments of NH_3 (1.46 D)
and NF_3 (0.2 D) is also instructive.
The electronegativity difference be-
tween nitrogen and fluorine is almost
the same as that between nitrogen
and hydrogen. But in NH_3 the bond
polarity is such that nitrogen is
negative and hydrogens are positive
while in NF_3 the fluorines are nega-
tive but nitrogen is positive. The direc-

FIG. 5.12. Build-up of dipole
moment in H_2O

tion of bond polarity in N-F is opposite to that in N-H but in both cases the contri-
bution of the lone pairs is in the same direction. The smaller dipole moment of
NF_3 is thus explained. CCl_4 has four carbon-chlorine bonds arranged in a symmetric

8

tetrahedral geometry around carbon and therefore despite each C—Cl bond being polar, the centres of gravity of all negative and positive ends coincide on carbon. CCl_4 is thus non-polar. $CHCl_3$ has a different composition and charge distribution and hence the molecule is polar. The arrows in Fig. 5.12 and Fig 5.13 point towards the centres of negative charge. An interesting comparison can be made between CO_2 and SO_2. While CO_2 has a zero dipole moment SO_2 has a good value. CO_2 is a linear molecule while SO_2 is a bent one. Although there is a lot of difference in the electronegativities of carbon and oxygen, the two bond polarities of the two carbon-oxygen bonds act in opposite direction. Hence the resultant effect is zero. In SO_2 the resultant of the two sulphur-oxygen bonds act in opposition to the

FIG. 5.13. Polarity of CCl_4 and $CHCl_3$: arrows indicate the direction of the centre of negative charge

lone pair polarity. But the bond polarity is more than the lone pair polarity and hence the molecule has a non-zero dipole moment. In paradichlorobenzene the two C—Cl bond polarities act in opposite direction and hence it has no dipole moment. But chlorobenzene or orthodichlorobenzene has a dipole moment, the latter having a higher value

We can utilise dipole moment data to gain an insight into the partial ionic/covalent character of a heteronuclear diatomic molecule. HCl has a dipole moment 1.03×10^{-18} esu cm and its bond length is found from Table 4.5 to be 1.27×10^{-8} cm. Taking the H—Cl bond length as the distance between the two charges, the charge ($\delta+$ or $\delta-$) is then calculated as 0.8×10^{-10} esu. If HCl were a purely ionic compound the charge on H and on Cl would be $+1$ or -1 ($= 4.8 \times 10^{-10}$ esu). Then we have:

$$\text{ionic character in HCl} = \frac{0.8 \times 10^{-10} \, esu \times 100}{4.8 \times 10^{-10} \, esu} = 17\%$$

Thus HCl is largely a covalent compound. On the other hand LiH has a dipole moment of 5.9 D and a bond length 1.60 A. We can calculate a 77% ionic character indicating that the compound is predominantly ionic. Such simple calculations show the per cent ionic character to fall in the series of hydrohalides as: HF, 46%; HCl, 17%; HBr, 12%; and HI, 5%. Note this is also the order of decreasing electronegativity from fluorine to iodine (section 4.3; Fig. 4.3). Note that the dipole moment rapidly falls from HF to HI although the bond length increases appreciably in the same direction. This indicates that the charge (due to electronegativity difference) plays a more dominating role than the distance i.e. the bond length ($\mu = \delta \times d$).

Dipole moment measurements often help to decide cis-trans isomerism in coordination complexes. $(R_3P)_2PtCl_2$ and $(R_3As)_2PtCl_2$ complexes have been isolated in α and β forms. The α-forms have recorded zero dipole moments and must therefore have collinear Pt—Cl and Pt—As (or Pt—P) links, that is, a trans structure. The β forms have high dipole moments and are cis isomers.

5.5. THE NATURE OF THE INTERMOLECULAR FORCES

Besides the primary forces responsible for the formation of molecules and ionic compounds there are secondary forces that operate between molecules. Although these molecular forces have not been defined as chemical bonds, this is the right place to discuss them briefly. Such intermolecular forces are popularly called van der Waals forces.

Unlike covalent bonding which is associated with orbital overlap at short internuclear distance van der Waals forces may operate at longer distances where no orbital overlap can occur. Hence such forces are weak. But they are the most universal. There are several types of forces that contribute to van der Waals attraction.

Dipole-dipole interaction. When the interacting atoms differ significantly in their electronegativity the resulting molecule is often a polar covalent compound (eg: ICl). Thus ICl will have a partial (δ^+) character on the iodine and a partial (δ^-) on the chlorine side of the molecule. These polar charges may be compared to the charges on NaCl, in which very much great difference in electronegativity leads to a complete transfer of electron from sodium to chlorine, giving a full $+$ and a full $-$ charge on the ions. In molecular ICl the dipoles so arrange themselves that a 'plus' end faces a 'minus' end and so on. This weak attractive force holds the molecules together. On application of little heat (M. P. ICl, 27°C) the weak van der Waals forces are no longer able to hold the molecules in rigid alignment and the compound melts. The weak forces still remain significant to maintain a liquid phase, where the molecules are still relatively close. On further heating the liquid boils and the van der Waals forces become really very insignificant.

A very special type of dipole-dipole interaction exists in some associated hydrides like NH_3, H_2O and HF. This special interaction has been named as hydrogen bond, and will be considered in the next section.

Instantaneous dipoles interaction: Since permanent dipoles do not exist in homonuclear diatomic molecules H_2, Cl_2, I_2 etc. a different type of attractive force must be postulated to explain the liquid and solid state of such substances.

Over a period of time the two bonding electrons in H_2 molecule are as close to one nucleus as to the other (compare the resonance forms). The molecule therefore does not possess any permanent dipole. But any given moment the electron density may be concentrated at one end of the molecule. A fraction of a second later this may be concentrated at the other end of the molecule. Thus instantaneous dipoles are created. These instantaneous dipoles induce similar dipoles in neighbouring molecules. These instantaneous dipoles lead to an attractive force between the molecules.

The strength of such induced dipoles interaction depends on the polarisability of the molecule. The ease of polarisation again depends on the size of the molecule. Large molecules are easily polarised than the small ones. Hence the bigger the molecular size and molecular weight, the more effective the polarisation is. Boiling points and melting points of covalent molecules are thus found to be functions of molecular size and molecular weight.

Ion-dipole interaction: Negative ends of dipolar molecules like H_2O, NH_3 may be attracted towards metal ions to form metal hydrates or metal ammoniates. The weak interaction occurs due to the lone pair electron density of H_2O or NH_3 facing the cations. So long as the attraction remains poor we get hydrates or ammoniates. When the attraction becomes formidable the cation and the above dipolar molecules are engaged in a far stronger bonding in the first sphere of attraction, and an aquo-metal or ammine-metal complex results. Ion-dipole interaction is responsible for the dissolution of ionic compounds in polar solvents.

Dipole-induced dipole interaction: This type of weak interaction exists between a molecule with a permanent dipole and a molecule (or atom) without one. The polar molecule may distort the electron density of the second molecule (or atom) towards its positive end so that the centres of positive and negative charge in the second molecule (or atom) does not coincide as in the absence of the polar molecule. Thus a dipole is induced. An attraction can now result between the permanent dipole and the induced dipole. The forces responsible for the formation of noble gas hydrates are of this class.

Ion-induced dipole interaction: Distortion of the electron density of large polarisable molecules may be effected also by a charged ion. Further interaction may take place between the ion and the induced dipole, even leading to the formation of a new entity. Interaction of halide ions and halogen molecules leading to polyhalide ions is considered to be of this type.

5·6. THE HYDROGEN BOND

By virtue of its having a single electron in the 1s orbital, hydrogen is capable of forming a single covalent bond. However, when it is covalently bonded to a strongly electronegative element the bond becomes strongly dipolar. The positive hydrogen end of the dipole can weakly link some other negative dipolar end present in the same very molecule or in another molecule, thus effectively forming a weak bond to a second electronegative atom. This weak, secondary bond between two electronegative elements through the agency of partially positive hydrogen is known as hydrogen bond.

FIG. 5.14. Boiling Points of covalent hydrides of group IVB to VIIB elements.

We enumerate below some examples where hydrogen bonding leads to special properties:

1. *Abnormal boiling point of binary hydrides:* The general expected trend of increase in melting points and boiling points of binary covalent hydrides with

increasing atomic number in a group is heavily violated by ammonia in group V, water in group VI and hydrogen fluoride in group VII. The plots of boiling points of the hydrides of group IV, V, VI and VII against Period number is shown in Fig. 5.14. The hydrides of carbon, silicon, germanium and tin are regular in the sense that the boiling points are functions of molecular weights. In each of the groups V, VI and VII the second, third and the fourth hydrides are regular in their boiling points but the first exhibits abnormal behaviour.

The abnormal behaviour of NH_3, H_2O and HF is due to association in liquid phase. This association is a consequence of hydrogen forming a special link or bond between polar covalent molecules. In binary hydride of a strong electro-negative element the bond between hydrogen and the parent element is an electron-pair covalent bond. Due to the high electronegativity of the parent element hydrogen develops a positive polarity and the parent element a negative polarity. The residual (fractional) positive charge on the hydrogen confers on it an extra ability to drag the negative end of a second hydride molecule and so on. The result is an associated liquid.

Hydrogen can thus form a special kind of bond, called hydrogen bond, to another electronegative atom of a second molecule or to a second electronegative atom of the same molecule.

2. *Abnormal heat of vapourisation of binary hydrides:* Compared to other liquids in which there are no hydrogen bonds but only universal van der Waals forces it is no wonder that H_2O will have a larger heat of vapourisation. In fact, the heat of vapourisation of H_2O at its boiling point is 9.72 KCal/mole, which is almost double that of H_2S. Such abnormality in heats of vapourisation is also seen for NH_3 in group VB and for HF in group VIIB. On plotting the heats of vapourisation of the hydrides of Groups IVB, VB, VIB and VIIB against Period numbers a plot like Fig. 5.14 is obtained.

3. *Dimerisation of acetic acid:* Structure determination of acetic acid reveals a dimer through intermolecular hydrogen bonding (5-1).

4. *Modification of acid character:* o-Hydroxybenzaldehyde and o-nitrophenol have their hydrogen bonding restricted within the molecules (intramolecular hydrogen bonding). Such hydrogen bonding may lead to a weakening of the acid character of the compound. However the K_A's of o-nitro-, p-nitrophenol and phenol are 600×10^{-10}, 690×10^{-10} and 1.3×10^{-10}. Nitrophenols are stronger acids than phenol because of electron withdrawing effect and resonating influence of the nitro group.

$$CH_3-C \begin{array}{c} O...H-O \\ \\ O-H...O \end{array} C-CH_3$$
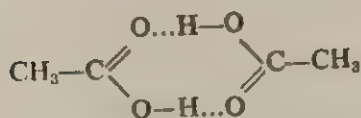
(5—I)
intermolecular hydrogen bonding
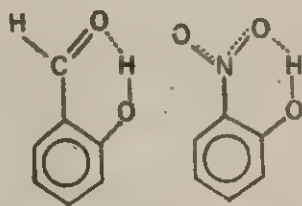
(5—II)
intramolecular hydrogen bonding

5. *Binding of Water in some hydrates:* Copper (II) sulphate forms a penta-hydrate. Four water molecules are coordinated to copper (II) in the first sphere of attraction. The fifth H_2O is hydrogen bonded between a sulphate group and a coordinated H_2O (cf. 29-II). While the coordinated water molecules can be removed at 150-200°C the removal of the fifth occurs with decomposition of the compound. The seventh water molecule of the true vitriols $NiSO_4.7H_2O$. $CoSO_4$. $7H_2O$ etc. is likewise hydrogen bonded.

6. *Abnormal solubility:* Organic compounds with strongly electronegative oxygen and nitrogen being present in functional groups are, in general, more soluble in $CHCl_3$, $CHCl_2F$ or CH_2Cl_2 than in CCl_4. This behaviour has been ascribed to the ability of the former group of solvents to form hydrogen bonded species with oxygen—and/or nitrogen of the organic solute compound.

X-ray and infra-red evidence. X-ray diffraction studies generally cannot locate the position of hydrogen atoms but can establish quite precisely other bond distances in a compound. Such structural studies have shown that the distance between two electronegative elements (X in X—H...X) of nearest hydrogen bonded molecules is shorter than the distance for comparable non-hydrogen-bonded molecules. Thirdly there is good infra red evidence as well. In case of hydrogen bonding, X—H bond goes over to X—H...X and this means that H...X bond being larger than X—H bond introduces some less-than-single bond character in the overall bond length between X and H. This is shown by a lowering of the X—H stretching frequency in hydrogen bonded compounds as compared to parallel non-hydrogen bonded compounds.

Strength of Hydrogen Bond: The strength of the hydrogen bond is directly related to the electronegativity of the parent element. With increasing electro-negativity the strength of the hydrogen bond increases from ammonia through water to hydrogen fluoride. The electronegativity difference is also the reason for a sharp weakening of the bond down a group. Thus hydrogen bonding in H_2S is much weaker than in H_2O, which is strikingly revealed by H_2S being a gas at ordinary temperature whereas H_2O, with a lower molecular weight, is a liquid.

The effect of size is shown by a comparison of NH_3 and HCl. Nitrogen and chlorine have the same electronegativity but chlorine is bigger in size than nitrogen (atomic radius: N, 0.70A; Cl, 0.99A). Ammonia is far strongly hydrogen-bonded (cf : Fig. 5.14) than hydrogen chloride.

Nature of the Hydrogen Bond: Since hydrogen has just one $1s$ orbital with a maximum electron capacity of two electrons it cannot form two simultaneous covalent bonds like F—H—F. This structure would impose four electrons in the $1s$ orbital or put two electrons on the much higher energy $2s$ or $2p$ orbital making the second bond very unstable. The structure must be considered as arising out of electrostatic attraction and also as a resonance hybrid of forms like the following:

$$[F^{\delta-}—H^{\delta+}...F^{\delta-}] \quad : \quad [F—H:F^-] \longleftrightarrow [F:H—F]$$
electrostatic attraction   Resonance
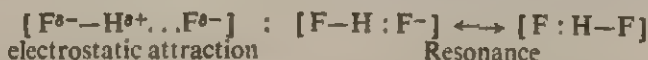
Although hydrogen bond falls in the same energy range (below 10 Kcal/mole)

as does van der Waals forces it seems to be formed in preferred direction. van der Waals forces, in general, are non-directional.

Hydrogen bonding, a chemical curiosity, is of importance to our very existence in this world. In the absence of hydrogen bonding water would be a gas at ordinary temperature and imagine there would exist no animal or vegetable life

Structure of Ice and Water and consequent influence on density: X-ray crystallographic study of ice reveals that each oxygen atom of H_2O is tetrahedrally surrounded by four other oxygen atoms. Each oxygen pair has in between them a hydrogen atom. This structure extends in all three directions in space, A lot of vacant space exists in between the oxygen tetrahedra. Because of the very effective hydrogen bonding there are present huge number of small holes in the structure. This structure explains why ice has a relatively low density.

On melting much of the above structure of ice is destroyed. Hydrogen bonding gets weaker and the liquid water consists of smaller ice-like units alongwith single H_2O molecules. The water molecules in the liquid state can pack themselves closer than in ice. Thus the density of water is greater than that of ice. The breaking down of the ice structure is very important in the temperature range 0°C and 4 C. But above 4°C increased molecular motion leads to expansion in volume of liquid water leading to a decrease in density.

STUDY QUESTIONS

1. Helium and other noble gases do not form diatomic molecules. Use valence bond theory to explain this behaviour. According to M.O. theory if we had He_2 we have to put two electrons in bonding 1s M.O. and two in the antibonding 1s σ*M.O., thus leading to no stability. Do you agree?

2. Why do we consider KCl as an ionic solid?

3. What are the chief factors that govern melting points and boiling points?

4. Apply Fajans' rules to classify the following compounds into ionic and covalent ones:

$$SiCl_4, CaCl_2, MgO, TeF_6, NH_3, CCl_4, InCl_3$$
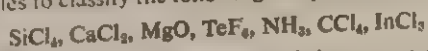
5. Elementary carbon has covalent links and yet it has an extraordinarily high sublimation point. Comment.

6. Diagonal relationship does not extend beyond the first two short periods. Comment.

7. Why is the boiling point of argon greater than that of neon? H_2S has a higher molecular weight than H_2O and yet is a gas at room temperature while H_2O is a liquid. Discuss.

8. The halides of boron and silicon coordinate with trimethylamine but those of carbon do not. Comment. (see also Chapter 17).

9. Explain why in a series of covalent compounds a bromide usually has a high boiling point than a chloride, while in a family of ionic compounds the reverse holds.

10. A naked proton cannot survive and has to be solvated. Explain and confirm from experimental facts (see also Chapter 8).

11. Comment on these dipole moments: (a) SO_2, 1.61D; CO_2, 0.00D. (b) NH_3, 1.49D; NF_3, 0.2D.

12. The addition of a second electron to an oxygen atom is not a favourable process, yet we find a number of ionic oxides. Comment.

13. For each of the following pairs indicate which substance is expected to be more covalent: $MgCl_2$ or $BeCl_2$; $CaCl_2$ or $ZnCl_2$; $CaCl_2$ or $CdCl_2$; ZnO or ZnS; $TiCl_1$ or $TiCl_4$; NaI or CsO

14. "Stannous tin is metallic while stannic tin is non-metallic." Comment.

15. Draw 'electron dot' formulas and 'dash' formulas for (a) BCl_3 (b) CH_3Br (c) CH_3OH (d) NF_3 (e) F_2O (f) $POCl_3$.

16. Explain in terms of the electronic arrangement of the noble gases the tendency of some atoms to lose electrons and the tendency of other atoms to gain electrons. How ionisation potential and electron affinity of atoms help in predicting this tendency.

17. State evidences in support of the following:

(a) C—Cl bonds in CCl_4 are covalent

(b) CaF_2 has ionic bonds

(c) bonds in sodium are metallic in nature

18. Write explanatory notes on:

(a) sigma and pi bonds (b) hybrid orbitals (c) bond multiplicity, bond length and bond energy (d) bonding and and antibonding orbitals.

19. Compare the bond energies and bond lengths in the following cases:

(a) N—N versus N $=$ N (b) O—O versus O $=$ O (c) O $=$ C $=$ O versus C$\equiv$ O

20. State the nature of the hybrid orbitals and the number of sigma and pi orbitals likely to be present in the following compounds:

(a) CH_4 (b) C_2H_4 (c) C_2H_2 and (d) CO_2

21. Explain: (a) dissociation energy of O_2 is less than that of O_2^+, but dissociation energy of N_2 is greater than that of N_2^+ (b) bond dissociation energy of NO is less than that of N_2 (c) NO and O_2 are both paramagnetic.

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Structure of Ionic Compounds and Shapes of Covalent Molecules

Having gained some familiarity with the nature of the chemical bonds, we discuss in this Chapter the structure of ionic compounds, and shapes of simple covalent molecules. It will be shown that for ionic compounds the ratio of the radii of the oppositely charged ions is the major factor that decides a particular ionic structure. Entirely different considerations apply to covalent molecules. Two models will be described to help predict the shapes of simple covalent molecules.

6.1. STRUCTURE OF IONIC COMPOUNDS

6.1.1. Radius Ratios and Preferred Structures of Some Ionic Compounds.

As described in the previous chapter the force of electrostatic attraction between oppositely charged ions constitutes the ionic bond. Since such bonds have Coulombic origin, each particular ion will tend to drag as many oppositely charged ions as possible around itself. The number of anions that surround a cation is called the coordination number of the cation and vice versa. Two factors appear important for an ionic structure:

(1) each ion assumes as large a coordination number as possible
(2) attraction between opposite ions in the limiting case just leads to cation-anion contact and to anion-anion contact. Any squeezing of the ions beyond the 'contact' positions will break down the structure.

These factors indicate that the size of the ions or better still the ratio of the radii of the cations and anions is the criterion that can strike a balance between the above two factors. It is therefore no wonder that similar AB type ionic compounds like CsCl, NaCl, ZnS do not crystallise with the same structure. Sodium ion (or chloride ion) in sodium chloride has a coordination number six, and in

ion (or chloride ion) in caesium chloride has a coordination number eight, and zinc ion (or sulphide ion) in zinc sulphide has a coordination number four.

We now work out the critical radius ratio, that is, the ratio of the cation, r^+, and the anion, r^-, for the above three common ionic crystal structures.

(a) In sodium chloride (Fig. 6.1) each sodium ion has six chloride ions as near neighbours. Four of these chloride ions in the limiting case of anion-anion contact, will touch the cation in the plane of the paper. The fifth and the sixth chloride ions will be above and below the plane of the paper, again in contact with the sodium ion. Assuming the ions to be hard spheres, it is easy to see from the geometry of the figure that the following relations hold in the limiting case of anion-anion contact and anion-cation contact.

FIG. 6.1. A section of NaCl structure showing the limiting case of anion anion contact

$$AB = BC = 2r^-$$

$$AC = 2r^- + 2r^+$$

Again $AC^2 = AB^2 + BC^2 = (2r^-)^2 + (2r^-)^2 = 8(r^-)^2$

$$\therefore AC = 2\sqrt{2}\,r^-$$

So that $2r^- + 2r^+ = 2\sqrt{2}\,r^-$; $\therefore 2r = 2\sqrt{2}r^- - 2r^- = 2r^-(\sqrt{2}-1)$

Whence $r^+/r^- = \sqrt{2}-1 = 0.414$

So the critical radius ratio at 'contact' position for NaCl structure is 0.414. In order that a 'safe' structure may be assumed r^+/r^- ratio should exceed 0.414 as otherwise the anion will have to be squeezed.
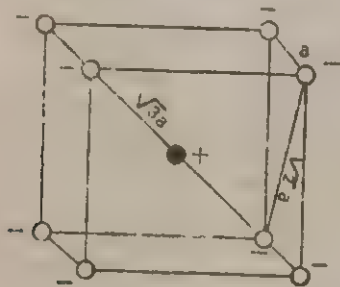
FIG 6.2. A section of CsCl structure
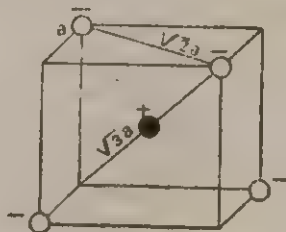
FIG 6.3. A section of ZnS structure

(b) In the structure of caesium chloride each caesium ion is surrounded by eight chloride ions and vice versa. Remembering the relation between the sides and diagonal of a cube (Fig. 6.2) it can be shown that the following relations will hold at the critical point of anion-anion contact and of cation-anion contact.

$$2(r^+ + r^-) = \sqrt{3}a$$

$2r^- = a$, where a = side of the cube.

$$\therefore 2r^+ + 2r^- = 2r^+ + a = \sqrt{3}\bar{a}; \quad \therefore 2r^+ = a(\sqrt{3}-1)$$

Then $r^+/r^- = \sqrt{3}-1 = 0.732$. *An ionic compound crystallising with CsCl structure will be stable only when the r^+/r^- ratio exceeds 0.732.*

(c) In zinc sulphide each zinc ion is tetrahedrally surrounded by four sulphide ions and vice versa. Again taking a cube and remembering that alternate corner points of a cube gives a tetrahedron (Fig. 6.3) we have the following relations at the critical point of anion-anion contact and anion-cation contact.

$$2(r^+ + r^-) = \sqrt{3}\,a$$

$$r^+ + r^- = \frac{\sqrt{3}a}{2} \text{ and } 2r^- = \sqrt{2}a : \quad r^- = \frac{\sqrt{2}a}{2} : \quad \therefore r^+ = \frac{\sqrt{3}}{2}a - \frac{\sqrt{2}}{2}a$$

$$\frac{r^+}{r^-} = \tfrac{1}{2}\sqrt{6}-1 = 0.225$$

Thus the optimum radius ratio for ZnS structure is 0.225–0.414, for NaCl structure 0.414–0.732, and for CsCl structure the ratio is above 0.732. The validity of these radius ratios is shown by examining a large body of ionic compounds in Table 6.1.

Table 6.1. Radius Ratios and Preferred Structures of Some Ionic Compounds

Compound	r^+/r^-	Structure
NaCl	0.52	NaCl type
NaI	0.44	,,
RbI	0.69	,,
KCl	0.74	,,
CsBr	0.87	CsCl type
CsI	0.78	,,
ZnS	0.40	ZnS type
ZnSe	0.37	,,
CuI	0.23	,,

We conclude our discussions on ionic crystals by remarking that in simple ionic compounds geometrical considerations largely determine the crystal structure.

● Na or Cl;   ● Cs or Cl;   ● Zn or S; ○ S or Zn
○ Cl or Na   ○ Cl or Cs
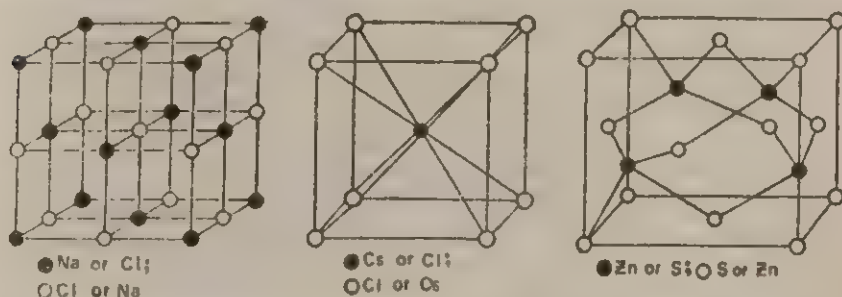
FIG. 6.4. The sodium chloride, caesium chloride and zinc blende structures

The critical radius ratio (cation/anion) gives the limiting condition that the cation is in contact with the maximum number of anions geometrically possible, and anions also are in contact with each other. Chemical considerations are unim-

portant for attainment of a particular structure. Thus chemically similar compounds may have quite different crystal structures. Conversely it may so happen that chemically dissimilar compounds will crystallise with the same ionic structure. Fig. 6.4 shows the three crystal structures discussed above.

6.1.2. Hexagonal Close Packing and Octahedral and Tetrahedral Holes: In hexagonal close packing of spheres each sphere is surrounded by six others (Fig. 6.5(a). These spheres touch each other and also touch the central sphere. Such a layer creates tetrahedral holes when another such layer is placed over the first layer such that a sphere of the second layer sits over the centre of the triangle formed by the contact of three spheres of the first layer. Besides the tetrahedral holes there are also octahedral holes between the layers [Fig. 6.5(b).
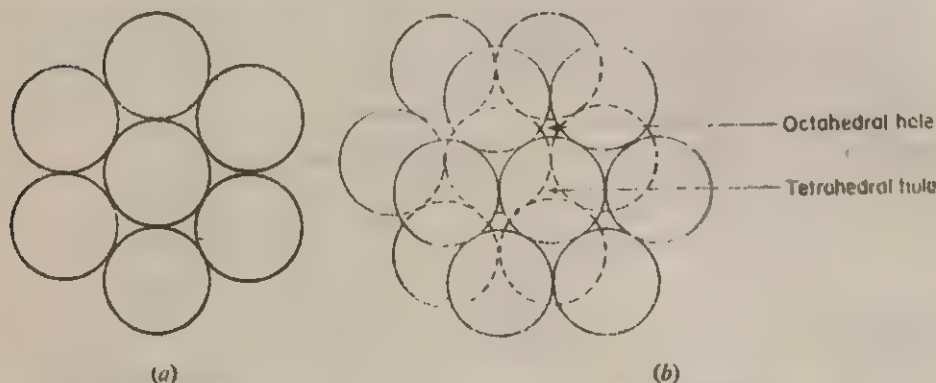
(a)   (b)
Fig. 6.5. (a) Hexagonal close   (b) Tetrahedral and octahedral holes in
packing of spheres,   hexagonal close packing.

In interstitial carbides and nitrides the small carbon atom or the nitrogen atom occupy the octahedral holes created by the close packing of the transition metal lattice. We have already seen that for octahedral hole fitting the radius ratio rules predict that the cation/anion i.e. small ion/large ion ratio should be in the range 0.4 to 0.7. It follows that the optimum carbon/metal or nitrogen/metal radius ratios should be in the range 0.4 to 0.7. Structural studies on interstitial compounds show that the upper limit of the radius ratio is ~0.6. Taking the covalent (atomic) radius of carbon as 0.77A and that of nitrogen as 0.7A (Table 4.5) we find that acceptable radius of transition metal should be in the range 1.3 to 1.9 for carbides and 1.2 to 1.7 for nitrides. The atomic radii of Cr, Mn, Fe, Co, Ni are below 1.3A and hence they do not form any nitrides or carbides. On the other hand, Ti, Hf, W, Nb have their radii larger than 1.3A and thus they form interstitial carbides and nitrides (Chapters 17 and 18).

It follows from the above discussions that hydrogen atom (radius 0.37A) is much too small to make any effective fitting in the octahedral holes of any of the above transition metals. It is not surprising therefore that interstitial hydrides are so very unstable.

6.2. SHAPES OF COVALENT MOLECULES

The basic step involved in the formation of covalent molecules is the overlap of suitable orbitals of the reactant atoms. The covalent bond is localised and has directional property. When there are two or more covalent bonds in a molecule, it is an interesting exercise to predict the shape, that is, the angle between the bonds of the resulting molecule. Such exercise will reveal the worthiness of our models of covalent bonding.

In what follows two models will be described for the purpose. These are (a) orbital overlap model and (b) valence shell electron pair repulsion. The models are complementary in nature.

(a) *Orbital overlap model:* We first begin with a knowledge of the pure atomic orbitals, their shapes and relative geometries. Recall that an s orbital has spherical symmetry about the nucleus. The three p orbitals are equivalent and are at right angles to each other. Each p orbital extends along an axis running through the nucleus and each has two pear-shaped lobes on either side of the nucleus. One orbital can accommodate a maximum of two electrons with opposite spins.

Hydrogen and oxygen atoms in H_2O may be assumed to form two s–p bonds by the overlap of two p orbitals of oxygen by the s orbitals of the two hydrogen atoms as shown below:

O $\uparrow\downarrow$ $\quad$ $\uparrow\downarrow$ $\quad$ $\uparrow$ $\quad$ $\uparrow\downarrow$ $\quad$ $\uparrow$
           $1s$ $\quad$ $2s$ $\quad$ $2p_x$ $\quad$ $2p_y$ $\quad$ $2p_z$

H $\downarrow$
           $1s$

H $\downarrow$
           $1s$
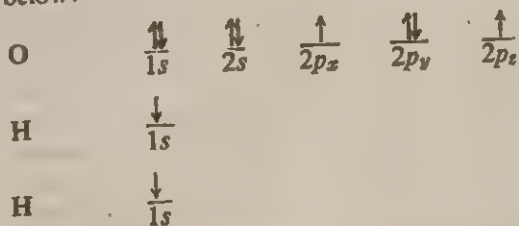
Since the two orbitals of oxygen, $2p_x$ and $2p_z$, are at right angles to each other, the overlap of these by the two spherically symmetric s orbitals of hydrogen can give rise to a molecule with the H—O—H bond angle as 90° (Fig. 6.6). The bond angle found experimentally in H_2O is 104°. Remembering that there is enough electronegativity difference between hydrogen and oxygen, the two hydrogen atoms will carry some residual positive charge and hence they are likely to repel each other thus expanding the H—O—H bond angle. But this would not amount to an expansion from 90° to 104°. Reaction of nitrogen and hydrogen gives NH_3. The model indicates overlap of three mutually perpendicular p_x, p_y, p_z orbitals of nitrogen by three s orbitals of three hydrogen atoms. The H—N—H bond angle (Fig. 6.6) is again predicted to be 90°. The experimental value is 107°. Here also the residual charges on the hydrogen atoms may lead to an H—N—H angle expansion but not to the extent observed.

The experimentally determined bond angles in H_2S, H_2Se, H_2Te, PH_3, AsH_3 and SbH_3 are nearly 90°, as is predicted by the model. The sulphur atom, compared to oxygen, is bigger in size (covalent radii are: O, 0.66 A; S, 1.04 A) and therefore the two H atoms are further apart in H_2S than in H_2O. Furthermore

the electronegativity difference between oxygen and sulphur is such as to make H less positive in H_2S than in H_2O. These factors minimise repulsion between the two H atoms and we get a better accord with experimental results in H_2S. Similar reasonings may be applied to H_2Se, PH_3, AsH_2 etc.
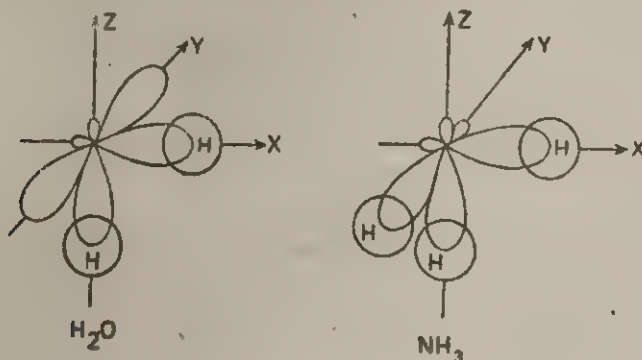
FIG. 6.6. Orbital overlap model for H_2O and NH_3

Instead of assuming overlap of pure atomic orbitals of the interacting atoms a modified approach is to adopt the concept of hybridised orbitals. Bond angle is then determined by the type of hybridisation. Thus sp, sp^2, sp^3, d^2sp^3 hybrid orbitals are linear, triangular, tetrahedral and octahedral respectively.

Hybridisation of the $2s$ orbital and the $2p_x$, $2p_y$ and $2p_z$ orbitals of oxygen leads to four equivalent, tetrahedral orbitals (sp^3). Six outer quantum shell electrons of oxygen are distributed as two pairs of electrons in two of these hybrid orbitals and one electron each in the remaining two tetrahedral orbitals. The last mentioned hybrid orbitals allow the $1s$ orbital of hydrogen to overlap giving sp^3-s type bonds in H_2O. Since the sp^3 orbitals are at $109°$ to each other, it is predicted that H—O—H angle will be $109°$ (experimental $104°$). A bond angle of $109°$ (experimental $107°$) is predicted for ammonia. It appears that compared to a model of pure orbital overlap, the agreement between the results of hybrid orbital model and experimental findings for H_2O, NH_3 is better but not excellent. It needs to be pointed out that so far we have neglected any repurcussion that the lone pairs of electrons in the molecule might have on the bonding pairs of electrons. Lone pairs repel the bond pairs more than the bond pairs repel bond pairs. This postulate will result in still better accord between theory and experiment.

Boron trichloride forms a triangular planar molecule with Cl—B—Cl bond angles $\sim 120°$. This shape is easily covered by assuming for boron an sp^2 hybridisation whereby the three hybrid orbitals will make an angle of $120°$ with each other in the same plane. The third p orbital is left out of hybridisation and is assumed to retain a p character. The three sp^2 orbitals then overlap with the unpaired electron in the p orbital of chlorine, thus making the Cl—B—Cl angle $\sim 120°$.

Beryllium fluoride forms a linear molecule with F—Be—F bond angle $\sim 180°$. This shape is predicted on assuming an sp hybridisation in beryllium.

However the hybrid orbital model, without further refinements, cannot explain the bond angles in molecules like H_2S, PH_3, AsH_3 etc.

(b) *The Valence Shell Electron Pair Repulsion Theory (VSEPR)*: This is a useful model for predicting the geometries of molecules of non-transition elements and also of symmetrical d°, d^5 and d^{10} transition metals. The theory is largely the work of Nyholm and Gillespie.

In all chemical combinations there occurs an interaction between outer orbital electrons of the reactants. The electrons belonging to the outermost quantum shell of the central reactant atom plus the additional electrons acquired as a result of bonding are called valence shell electrons. According to VSEPR theory the arrangement of the bonds around an atomic centre depends on the number of electron pairs surrounding the central atom and also on the relative size and shape of the orbitals which contain the valence shell electron pairs. The preferred arrangement of a given number of electron pairs in the valence shell of an atom is the one that maximises their distance apart. Each electron pair occupies a well defined region of space and other electrons avoid this space. For electron pairs in the same valence shell the preferred arrangements for 2 to 6 electron pairs which maximise the distance between electron pairs are given in Table 6.2. Note that the linear, triangular planar, regular tetrahedral, trigonal bipyramidal and regular octahedral arrangements of electron pairs with 2, 3, 4, 5 and 6 bonding pairs correspond respectively to the sp, sp^2, sp^3, sp^3d and d^2sp^3 hybrid orbitals in the valence bond theory.

By making additional postulates it is possible to explain small variations in bond angles and bond lengths from those predicted by theory. It needs to be noted that the electron pairs in valence shell are not all equivalent. They may bond different ligands, they may be unshared lone pairs or they may participate in multiple bonding. Some rules are now given to help explain the small variations in bond angles of certain common covalent molecules.

Rule 1. Lone pairs repel neighbouring electron pairs more than do bonding electron pairs. A lone pair is under the control of only one nucleus and therefore it is 'fatter' than a 'slimmer' bonding pair between two nuclei. The magnitude of repulsion between different electron pairs has the following order:

lone pair—lone pair > lone pair—bonding pair > bonding pair—bonding pair
(strongest)   (weakest)

An effect of these varying degrees of repulsion is exemplified by the bond angles in the series CH_4 (109°), NH_3 (107°) and H_2O (104°). Since CH_4 has all bonding pairs the H—C—H bond angle is ideal and tetrahedral. In NH_3 the lone pair repels the bond pairs more and H—N—H bond angle is squashed from 109° to 107°. Two lone pairs in H_2O squash the bond pairs still more, from 109° to 104°.

Rule 2. The repulsion exerted by the bonding pair decreases with increasing electronegativity of the B atom in AB_x molecules.

With increasing electronegativity of B the average position of the bonding pair moves farther from the central element A. Therefore the repulsive effect of the bonding pair on the electron pairs on A decreases with increasing electro-

Table 6.2. VSEPR Predicted Shapes of some Molecules

Number of electron pairs in valence shell	Predicted arrangement* of electron pairs in space	Number of bonding pairs	Number of lone pairs	Example	Shape
2	linear	2	0	$HgCl_2$	linear
3	triangular plane	3	0	BCl_3	triangular plane
		2	1	$SnCl_2$	V shaped
4	regular tetrahedron	4	0	CH_4	regular tetrahedron
		3	1	NH_3	Pyramidal
		2	2	H_2O	V shaped
5	trigonal bipyramid	5	0	PCl_5	trigonal bipyramid
		4	1	$TeCl_4$	irregular tetrahedron
		3	2	ClF_3	T shaped
6	regular octahedron	6	0	SF_6	Octahedron
		5	1	IF_5	Square pyramid
		4	2	XeF_4	Square planar

*The predictions have not taken into consideration the addtional postulates designed to achieve further accord with experimental bond angles.

negativity of B. Thus the B—A—B bond angle decreases with increasing electronegativity of B. Decreasing size of B (of the same group) will also have the same effect.

PCl_3	100	$AsCl_3$	98.4	NF_3	102	OF_2	103
PBr_3	101.5	$AsBr_3$	100.5				
PI_3	102	AsI_3	101.5	NH_3	107	OH_2	104.5

Rule 3. Repulsions between electron pairs in filled shells cause small changes in bond angles than the repulsions between electron pairs in incompletely filled shells.

The orbitals in a filled shell cover all the space around the central atom. Therefore any repulsive force designed to alter the bond angles in such filled shells is resisted. B, C, N, O and F of the first row of the Periodic Table have four orbitals in their valence shells, directed tetrahedrally. The repulsions in molecules with one or two lone pairs can at best change the bond angles by only a few degrees from 109° (compare NH_3, H_2O etc). On the other hand orbitals in an incompletely filled shell cannot make up for all the space around the central atom. As a result, repulsive forces exerted on the electron pairs of such shells are more significant and as a

consequence bond angles change by a larger extent. Elements of the second short period such as P, S or Cl have a maximum of nine orbitals (one s three p and five d) in their valence shell. In a compound like H_2S there are but eight electrons in the valence shell occupying four orbitals. Hence the repulsion exerted by the two lone pairs can alter the bond angle of H—S—H (92.2) by a larger extent than is possible by the lone pairs in H—O—H. Similarly H—P—H bond angle (93.8) is affected much more than the bond angle in H—N—H.

Rule 4. Multiple bonds exert greater repulsive effect on other orbitals than is shown by single bonds. Multiple bonds do not grossly affect the stereochemistry of a molecule.

Occurrence of a π-bond over and above a σ-bond decreases the bond length This means a double bond or a triple bond is considerably 'fatter' than a single bond. Therefore we would expect such a multiple bond to exert greater repulsive force on other orbitals. Examination of the XAX bond angles of the molecules given below shows that roughly they conform to the gross stereochemistry expected on the basis of lone pairs and bonding pairs (109° for expected tetrahedral OPF_3 and 120° for expected trigonal planar OCF_2). The multiple bond repels the other bonds so that XAX bond angle falls below that expected from the idealised geometry. It follows that the angle between the multiple bond and the other single bonds in the molecule will be greater than the angle between two single bonds of the molecule.

	<XAX			<XAX	<XSO	·· XCO
O = PF_3	102.5	O = CF_2	108°			124
O = PCl_3	103.5	O = CCl_2	111°.			124
O = PBr_3	· 108.0	S = PCl_3	100.5			
S = PF_3	100.3	S = PBr_3 .	106.0			
S = PCl_3	100.5	O = SF_2	92.3	106.8		
S = PBr_3 ·	106.0	O = SBr_2	96.0	108.0		

The VSEPR as developed above assumes that the inner shells of electrons are spherical and have no influence on the geometry of valence shell electron pairs. Thus the conclusions are valid for the main group representative elements and also for the spherical d^1, d^5 and d^{10} metals. The theory is not useful for predicting the shapes of transition metal complexes.

Problem: Predict the shape of nitrosyl chloride.

Nitrosyl chloride is ClNO. The central element nitrogen is linked to chlorine through a single bond and to oxygen via a double bond. Hence the valence shell of nitrogen has $5 + 1 + 2 = 8$ electrons. There are three bond pairs and one lone pair. The pi bond between nitrogen and oxygen does not influence the shape of the molecule. Thus the two sigma bond pairs and the lone pair should roughly be at 120°. Since lone pair repels bond pairs more strongly the bond angle < ClNO should be less than 120°. In fact the bond angle is about 116°. It is V-shaped.

Problem: Predict the shape of sulphuryl (sulphonyl) chloride

Sulphuryl chloride is SO_2Cl_2. The central element sulphur is bonded to the two chlorines via single bonds and to the two oxygens via double bonds. Then valence shell of sulphur has $6 + 1 + 1 + 2 + 2 = 12$ electrons. Of the six electron pairs the two pi bond pairs will not influence the shape of the molecule. So we are left with four electron pairs which are all bond pairs. A tetrahedral structure follows.
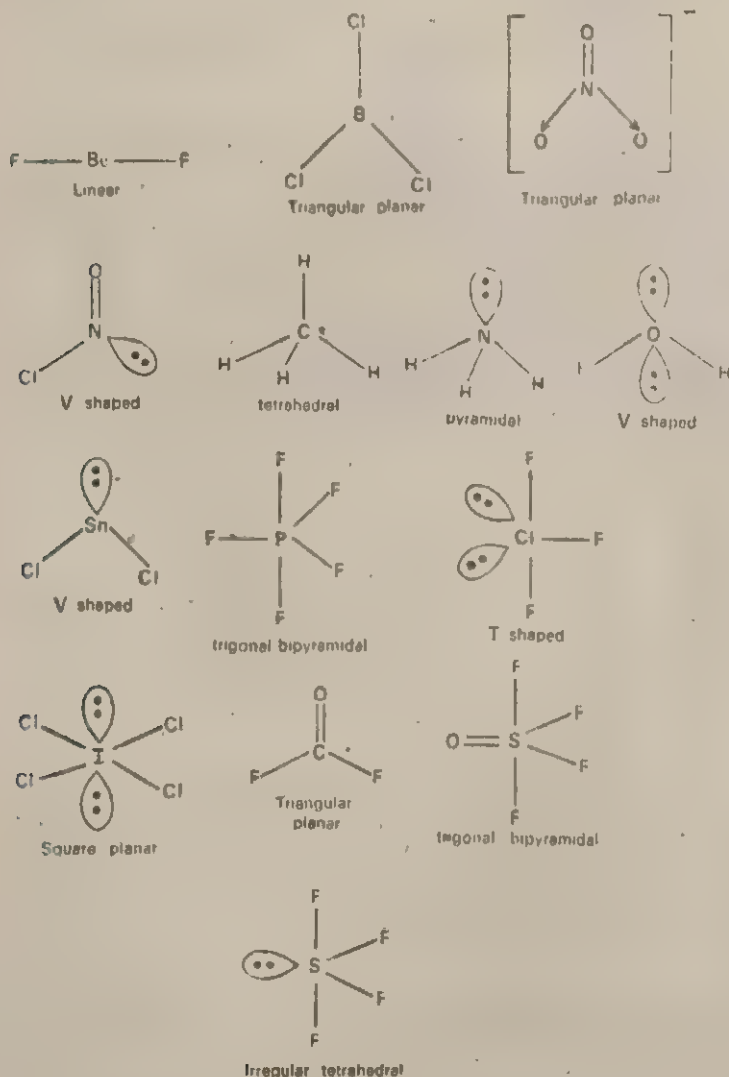
FIG. 6.7. Shapes of some molecules and ions

Alternatively we may assume that the two oxygens are linked via coordinate bonds from sulphur. Then the valence shell of sulphur has $6 + 1 + 1 = 8$ elec-

trons. Thus there are four bond pairs leading to a tetrahedral shape for the compound.

Problem: Predict the shape of chlorate ion.

Chlorate ion is $ClO_3{}^-$. The central element chlorine is bonded to the three oxygen atoms through coordinate covalent bonds. The valence shell of chlorine is made up of $7 + 1 = 8$ electrons i.e. four electron pairs. Of these four pairs three are bond pairs and one lone pair. Therefore the molecule will have a pyramidal shape like NH_3.

Problem: Predict the shape of carbonium ion.

A carbonium ion is formed as a result of, say, heterolytic cleavage of a carbon halogen bond. The carbon electron goes over to the halogen making a halide ion and a positive carbonium ion like $(CH_3)_3C^+$ and X^-. The valence shell of the central carbon has $3 + 3 = 6$ electrons, which make the $C - C$ bond pairs. It follows that the three bond pairs will attain maximum stability when they are at $120°$ in a plane i.e. the shape will be a flat triangular planar one.

On the hybridisation model the central carbon is assumed to be sp^2 hybridised with the third (say p_z) orbital being empty. The three unpaired electrons in the three sp^2 hybrid orbitals then will overlap with suitable orbitals having electrons with opposite spin. Once again the shape turns out to be a triangular planar one.

Problem: Predict the shape of carbanion.

A carbanion has three shared pair covalent bonds and a lone pair. The shape will then be pyramidal (cf. NH_3), one of the three vertices of a tetrahedron being occupied by the lone pair.

On the hybridisation model carbon is sp^3 hybridised.

Problem: Explain the T shape of ClF_3.

The valence shell of the central element chlorine has $7 + 1 + 1 + 1 = 10$ electrons i.e. five electron pairs. Of these three are bond pairs and two lone pairs. A trigonal bipyramidal arrangement is expected. According to rule I of VSEPR the two lone pairs should take up the two axial positions. But it is an empirical fact that lone pairs prefer to take up equatorial positions. Lone pairs are fatter than bond pairs and this fact probably prompts the lone pairs to occupy equatorial positions. Thus in ClF_3 two lone pairs and one fluorine take up the equatorial plane while the other two fluorine occupy apical sites. In such an environment each equatorial lone-pair feels two $90°$ repulsion and one $120°$ repulsion with the bond pairs. If the lone pairs occupied axial positions then each had to face three $90°$ repulsion with the three equatorial bond pairs. Experimental structure determination reveals that a lone pair prefers two $90°$ repulsions and one $120°$ repulsion. However this explanation is not beyond criticism.

BrF_3 has a shape like that of ClF_3.

STUDY QUESTIONS

1. Use a simple ionic model to predict the shapes of CO_2, NH_3, BCl_3, $BeCl_2$, $HgCl_2$, $PbCl_2$. Compare the results with VSEPR model (see also Chapter 10).

2. In a close packed type crystal structure the octahedral holes can be occupied by spheres of radius $0.41\ r$ and tetrahedral holes by spheres of radius $0.225\ r$ ($r =$ radius of the spheres making the holes). Comment.

3. Which of the following in each pair will have the larger bond angles?

$$CH_4,\ NH_3;\ OF_2,\ OCl_2;\ NH_3,\ NF_3;\ PH_3,\ NH_3$$

4. Predict the shapes of XeF_2 and XeF_4 on the VSEPR model and also apply the hybridisation scheme. Check your results with Chapter 21.

5. Explain why transition metal hydrides are so very unstable while some such metal carbides and nitrides can be prepared.

6. Why the $\angle HOH$ bond angle is less than the tetrahedral angle of $109°$?

7. Predict the shapes of CCl_4 and $POCl_3$ molecules on the VSEPR model.

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Oxidation-Reduction Reactions

A better understanding of the electronic structure of elements, and of chemical reactions has led to an overhauling of our classical conceptions of oxidation and reduction. Studies of electrochemical reactions have provided a firm, quantitative basis of oxidation and reduction processes. Modern ideas on such processes allow us to foresee many chemical reactions and further help us to control many reactions according to our needs. A discussion of the basic ideas of oxidation-reduction (redox) reactions is presented in this Chapter.

7.1. ELECTRONIC CONCEPT OF OXIDATION AND REDUCTION

Oxidation has been classically defined as the combination of oxygen (or any other electronegative element) with another element or as the removal of hydrogen (or any other electropositive element) from chemical compounds. We know magnesium metal burns in oxygen to produce magnesium oxide. The same metal reacts with chlorine to produce magnesium chloride. In both instances magnesium is considered to have been oxidised.

An examination of the electronic structures of MgO and $MgCl_2$ reveals a common feature, namely both have doubly charged Mg^{2+} ions in their crystal lattice. The reaction of magnesium metal with either oxygen or chlorine has led to the removal of two electrons from a zerovalent magnesium metal resulting in the formation of Mg^{2+}.

$$2Mg + O_2 \rightarrow 2Mg^{2+} + 2O^{2-}$$
$$Mg + Cl_2 \rightarrow Mg^{2+} + 2Cl^-$$
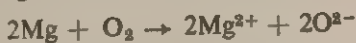
On the other hand the lost electrons have found new homes in oxygen or chlorine forming the oxide ion or the chloride ions. It would thus appear that the classical definition of oxidation has an intimate connection with the removal of electrons. The converse should hold for reduction. Thus *oxidation is a process which results*

in the loss of one or more electrons by atoms or ions. *Reduction is a process which results in the gain of one or more electrons by atoms or ions.* Therefore an oxidising agent is one that gains electrons and is then reduced to a lower valence. A reducing agent is one that loses electrons and is oxidised to a higher valence. In the above examples, magnesium metal is the reducing agent and oxygen (or chlorine) the oxidising agent.

7.2. OXIDATION NUMBER CONCEPT OF OXIDATION AND REDUCTION

The definition of oxidation and reduction based on loss or gain of electrons is limited in scope since the definition holds good only for ionic compounds. For example, the reaction between H_2 and O_2 leading to H_2O cannot be covered by the electronic concept since H_2O is not an ionic compound. It may be recalled that classically we could still say that hydrogen is oxidised to H O in the same sense as the burning of magnesium in oxygen is considered oxidation. Similarly H_2 and Cl_2 react to form a covalent molecule HCl. Classically hydrogen is oxidised (or conversely chlorine is reduced) but the resulting compound being a covalent one, the reaction cannot be covered by the electronic concept.

In order to cover such reactions also under oxidation-reduction the concept of oxidation number has been developed. *The oxidation number of an element in a compound is the formal charge (positive or negative) which would be assigned to the element, if all the bonds in the compounds were ionic bonds.* All compounds are treated as though they were ionic merely because of the ease in counting oxidation numbers. *The oxidation number therefore is arbitrary.*

Electronegativity concept is utilised in adducing a formal charge to an atom. The less electronegative of the partners of a binary compound is arbitrarily assigned a positive oxidation number and the more electronegative one a negative oxidation number. Fluorine, being the most electronegative, has always a negative oxidation number. The alkali metals are highly electropositive, have low electronegativity, and hence have been assigned positive oxidation numbers. Since in all their compounds the alkali metals behave consistently as unipositive ions, they are assigned oxidation number + 1. Similar reasoning would lead to an assignment of −1 to the halogens. In HF gas fluorine has an oxidation number of −1 and hydrogen is assigned an oxidation number of + 1.

The following general rules are to be observed for the assignment of oxidation numbers.

1. *The algebraic sum of the oxidation numbers of all the atoms in a compound must be zero.*

2. *Atoms of diatomic molecules like H_2, Cl_2, O_2 etc. or of metallic elements are assigned zero oxidation numbers since the same elements of similar electronegativity are involved in the bonding.*

3. *Oxygen has normally an oxidation number − 2. In H_2O_2 the oxidation number of oxygen is −1 since hydrogen has to be assigned −1. In F_2O oxygen has an oxidation number +2 because fluorine is more electronegative than oxygen.*

4. In all the metal hydrides, LiH, CsH etc, the oxidation number of hydrogen, for reasons of varying electronegativity, is −1.

When the above rules are applied the oxidation numbers of carbon in the compounds CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4 and CO_2 are −4, −2, 0, 2, 4 and +4 respectively. In H_2, the oxidation number of hydrogen is zero but in H_2O it is +1. Similarly magnesium in elementary state has a zero oxidation number but in $MgCl_2$, the number is +2. Hence *oxidation may be defined as a process in which an increase in oxidation number occurs.* Conversely, *reduction is a process in which a decrease in oxidation number occurs. A reagent which can increase the oxidation number of an element or ion is called an oxidising agent.* Similarly *a reagent that lowers the oxidation number of an element or ion is called a reducing agent.*

Oxidation and reduction are always found to go hand in hand during a redox reaction. Whenever an element or a compound is oxidised, another element or another compound must be simultaneously reduced. *An oxidant is reduced and simultaneously the reductant is oxidised.* A schematic representation of oxidation-reduction reactions based on (a) electronic concept and (b) oxidation number concept is given in Fig. 7.1.
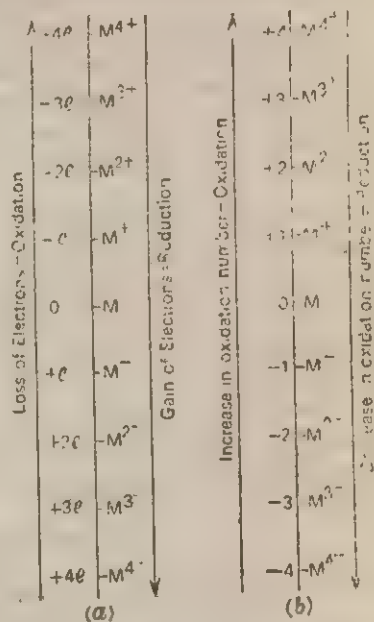
FIG 7.1. Schematic representation of oxidation and reduction on (a) electronic concept and (b) oxidation number concept

7.3. BALANCING OXIDATION-REDUCTION REACTIONS

It follows from our above discussions that we should be able to balance oxidation-reduction reactions on the basis of (1) electron loss or gain and (2) change in oxidation number. The first method is commonly known as ion-electron method. Certain general rules are described below for writing balanced redox reactions.

7.3.1. Ion-electron Method of Balancing Oxidation-Reduction Reactions: The following rules are useful:

(1) ascertain the reactants and products, and their chemical formulas.
(2) set up partial equations representing the reduction of the oxidant, and the oxidation of the reductant.
(3) if the reaction occurs in acid medium use requisite number of H^+ for balancing the number of atoms involved in the partial equation. For alkaline medium use OH^- ions.

(4) balance the charges in the partial equations by adding suitable number of electrons. These electrons indicate the electrons involved in the oxidation or the reduction half reactions.

(5) multiply each partial equation by a suitable factor so that each of the two partial equations involve the same number of electrons.

(6) add the partial equations and cancel out species which appear on both sides of the equations.

Some examples will now be given to elucidate the rules. It is known that in aqueous acid medium potassium permanganate oxidises ferrous ion to the ferric state. In this reaction permanganate ion is the oxidant and ferrous ion the reductant. The left hand side of the ultimate equation will carry MnO_4^-, H^+ and Fe^{2+} and the right hand side will have as products Mn^{2+}, H_2O and Fe^{3+} ions.

The partial equation representing the reduction of the oxidant MnO_4^- will involve $MnO_4^- \rightarrow Mn^{2+}$. Since the reaction occurs in acid medium we utilise eight H^+ ions to balance the four oxygen atoms of MnO_4^-, thus:

$$MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$$

Since the above partial equation is still unbalanced from the viewpoint of charge, the equation is balanced by bringing in five electrons:

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$$

Note that $MnO_4^- \rightarrow Mn^{2+}$ is indeed a five electron reduction ($Mn^{7+} \rightarrow Mn^{2+}$). If we now apply the above steps to obtain the partial equation representing the oxidation of the reductant we have the following:

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e$$

This equation on multiplication by 5 and then adding to the partial equation of the oxidant gives the final balanced equation:

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$$

$$\underline{5\,(Fe^{2+} \rightleftharpoons Fe^{3+} + e)}$$

$$MnO_4^- + 8H^+ + 5Fe^{2+} = Mn^{2+} + 5Fe^{3+} + 4H_2O$$
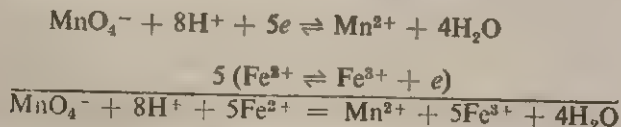
The second example relates to the oxidation of potassium iodide by potassium dichromate in dilute acid medium. In this reaction dichromate (chromium in +6 state) is reduced to chromium (III) and iodide ion is oxidised to elementary iodine. Taking the dichromate side, balancing the atoms and charges provides the partial equation:

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O$$

Considering the case of the iodide ion we get:

$$2I^- \rightleftharpoons I_2 + 2e$$

Multiplying this by 3 and adding the two partial equations we have the following final equation:

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O$$

$$3(2I^- \rightleftharpoons I_2 + 2e)$$

$$\overline{Cr_2O_7^{2-} + 14H^+ + 6I^- = 2Cr^{3+} + 3I_2 + 7H_2O}$$
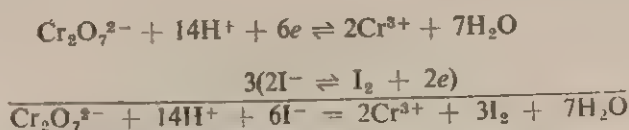
The third example is the reaction of permanganate ion with sodium stannite, Na_2SnO_2, in alkaline solution in which manganese dioxide MnO_2 and sodium stannate, Na_2SnO_3 are formed. The partial equation representing the reduction of the oxidant is $MnO_4^- \rightarrow MnO_2$. Since the medium is alkaline we put requisite number of OH^- ions to effect atom balance as:

$$MnO_4^- + 2H_2O \rightarrow MnO_2 + 4OH^-$$

To balance the charge on both sides three electrons are added on the left hand side:

$$MnO_4^- + 2H_2O + 3e \rightleftharpoons MnO_2 + 4OH^-$$

For the reductant the balanced partial equation is:

$$SnO_2^{2-} + 2OH^- \rightleftharpoons SnO_3^{2-} + H_2O + 2e$$
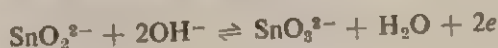
To balance the number of electrons on both sides, the first equation is multiplied by 2 and the second by 3 and on adding we have the final form of the ionic equation:

$$2MnO_4^- + 4H_2O + 6e \rightleftharpoons 2MnO_3 + 8OH^-$$

$$3SnO_2^{2-} + 6OH^- \rightleftharpoons 3SnO_4^{2-} + 3H_2O + 6e$$

$$\overline{2MnO_4^- + 3SnO_2^{2-} + H_2O = 2MnO_2 + 3SnO_3^{2-} + 2OH^-}$$
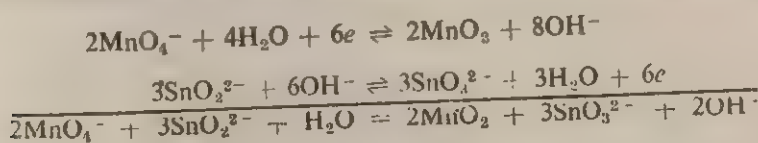
Proceeding as shown above we can represent the oxidation of Mn^{2+} to MnO_4^- by PbO_2 in acid solution as:

$$Mn^{2+} + 4H_2O \rightleftharpoons MnO_4^- + 8H^+ + 5e \quad [\times 2]$$

$$PbO_2 + 4H^+ + 2e \rightleftharpoons Pb^{2+} + 2H_2O \quad [\times 5]$$

$$\overline{2Mn^{2+} + 5PbO_2 + 4H^+ = 2MnO_4^- + 5Pb^{2+} + 2H_4O}$$
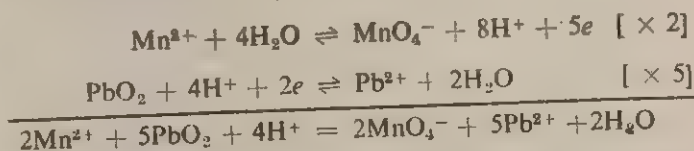
Oxidation of Mn^{2+} to MnO_4^- by $NaBiO_3$ in acid medium may be represented as:

$$Mn^{2+} + 4H_2O \rightleftharpoons MnO_4^- + 8H^+ + 5e \quad [\times 2]$$

$$BiO_3^- + 4H^+ + 2e \rightleftharpoons BiO^+ + 2H_2O \quad [\times 5]$$

$$\overline{2Mn^{2+} + 5BiO_3^- + 4H^+ \rightleftharpoons 2MnO_4^- + 5BiO^+ + 2H_2O}$$
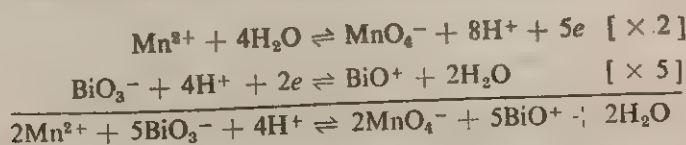
7.3.2. Oxidation Number Method of Balancing Oxidation-Reduction Reactions:

Assuming that the oxidation number of oxygen remains unchanged manganese

in MnO_4^- has an oxidation number $+7$. Calculation of the decrease and increase in oxidation number gives:

$$\underset{\text{oxidation number increases by 1}}{\underset{+7}{MnO_4^-} + \underset{+2}{Fe^{2+}} \rightarrow \underset{+2}{Mn^{2+}} + \underset{+3}{Fe^{3+}}}$$

oxidation number decreases by 5

oxidation number increases by 1
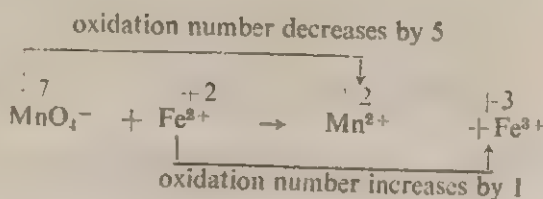
Putting right factors the decrease and increase in oxidation number are balanced, giving:

$$MnO_4^- + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+}$$

Since the reaction medium is acidic and the charges are not equal on the two sides of the above expression, H^+ ions are added and requisite number of H_2O written:

$$MnO_4^- + 8H^+ + 5Fe^{2+} = Mn^{2+} + 5Fe^{3+} + 4H_2O$$

The oxidation of iodide ion by dichromate ion in acid medium may likewise be balanced as follows:

(a) $Cr_2O_7^{2-} + I^- \rightarrow Cr^{3+} + I_2$

oxidation number decreases by $2 \times (+3)$

$2 \times (+6)$ $2 \times (+3)$

(b) $Cr_2O_7^{2-} + I^- \rightarrow 2Cr^{3+} + I_2$

oxidation number increases by 1

(c) $Cr_2O_7^{2-} + 6I^- \rightarrow 2Cr^{3+} + 3I_2$

(d) $Cr_2O_7^{2-} + 14H^+ + 6I = 2Cr^{3+} + 3I_2 + 7H_2O$
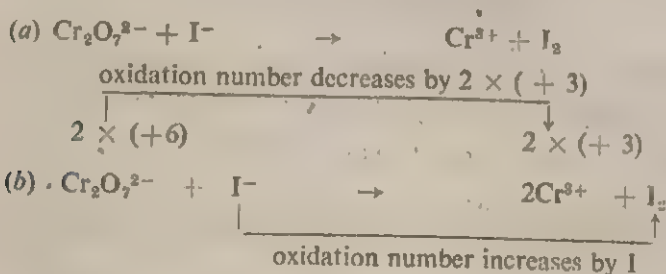
The third example of oxidation of sodium stannite to stannate in alkaline medium may be worked out as:

(a) $MnO_4^- + SnO_2^{2-} \rightarrow MnO_2 + SnO_3^{2-}$

oxidation number decreases by 3

$+7$ $+4$

(b) $MnO_4^- + SnO_2^{2-} \rightarrow MnO_2 + SnO_3^{2-}$

oxidation number increases by 2
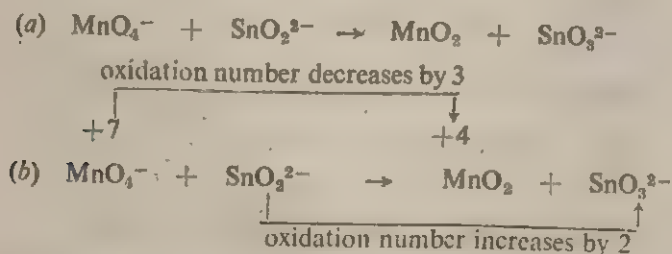
(c) equalising the increase and decrease in oxidation number:

$$2MnO_4^- + 3SnO_2^{2-} \rightarrow 2MnO_2 + 3SnO_3^{2-}$$

(d) because the medium is alkaline and because the ionic charges are not equal on the two sides, requisite number (2) of OH^- ions are added to the right hand side:

$$2MnO_4^- + 3SnO_2^{2-} \rightarrow 2MnO_2 + 3SnO_3^{2-} + 2OH^-$$

(e) Since there are two hydrogen atoms on the right and none on the left, H_2O is added to make atom balance. The final equation is:

$$2MnO_4^- \cdot 3SnO_2^{2-} + H_2O = 2MnO_2 + 3SnO_3^{2-} + 2OH^-$$

The oxidation of Mn^{2+} to MnO_4^- by PbO_2 is left out as an exercise

7.4. ELECTROCHEMICAL AND ELECTROLYTIC REACTIONS

7.4.1. Electrochemical Reactions:

It has been pointed out at the beginning of this chapter that studies of electrochemical reactions provide a quantitative basis of for oxidation-reduction reactions. Electricity and chemical change are intimately connected. Our entire concept of matter presumes that electronic structures are the best models for understanding the relation between matter and chemical change.

The Daniell cell, a typical example of an electrochemical cell (also known as voltaic cell or galvanic cell) consists of a copper electrode dipped in copper (II) sulphate solution and a zinc electrode immersed in zinc (II) sulphate solution. The two components are usually separated by a porous barrier thus minimising mixing of the two solutions. If the two metal electrodes are connected to a light bulb, the latter will glow indicating passage of electric current. *An electrochemical cell is a system of chemicals so arranged as to produce electric energy out of spontaneous oxidation-reducton reaction.* In the Daniell cell electrons are transferred from zinc atoms to copper (II) ions. Since as electrochemical cell consists of two electrodes of different characteristics it is of advantage to consider the two electrode reactions separately. The two electrode reactions of the Daniell cell are:

at the zinc electrode	at the copper electrode
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

over all reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
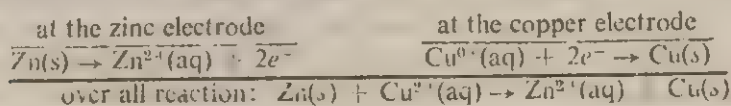
An equation describing the reaction at a single electrode of an electrochemical cell is called a half reaction. An electrode and the surrounding solution in the electrode compartment is called a half cell. Therefore the chemical change that takes place in a half cell is described by a half reaction. However, this needs to be emphasized that no half reaction can be separated out of the full reaction of an electrochemical cell. An equation for a half reaction represents the reaction imagined to occur at a particular electrode.

That electrode where oxidation (i.e. loss of electrons) occurs is called the anode. Conversely the electrode where reduction (i.e. addition of electrons) occurs is called the cathode. In the Daniell cell the zinc electrode is the anode while the copper electrode is the cathode. In the outer circuit electrons flow from zinc to copper.

The electric potential difference between the electrodes can be measured with the help of a voltmeter. It is possible to determine quantitatively the ability of one electrode to transfer electrons to another electrode in a cell. This ability of an electrode to transfer electrons is measured in relation to a single, selected electrode, serving as a reference electrode. The selected electrode against which all measurements are made is called the standard electrode.

A hydrogen electrode has been the standard reference electrode against which other single electrode potentials are determined. A standard hydrogen electrode consists of a platinum plate or foil, coated with platinum black, immersed in a solution of $H^+(aq)$ at a concentration of 1 M with H_2 gas being bubbled over the surface of the metal as shown in Fig. 7.2. at a pressure of 1 atmosphere and at 25°C. (Platinum black is deposited on a bright platinum cathode - a wire or a foil — when H_2PtCl_6 solution is electrolysed. A bright platinum foil or wire serves as the anode).
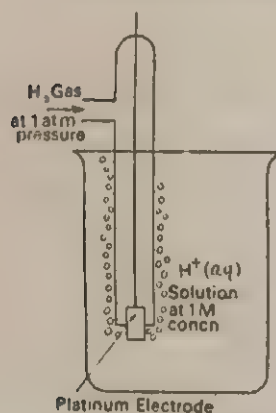
H₂ Gas
at 1 atm
pressure

$H^+(aq)$
Solution
at 1 M
concn

Platinum Electrode

FIG. 7.2. A standard hydro-
gen electrode

The half reaction at the hydrogen electrode is described by

$$H^+(aq) + e \rightarrow \tfrac{1}{2}H_2(g)$$

This half cell includes hydrogen ion in aqueous solution, H_2 gas and an inert platinum plate to make contact with $H^+(aq)$, H_2 gas and the solution. The platinum plate provides a conducting path for electron transfer and permits an equilibrium to be established between $H^+(aq)$ ions and hydrogen atoms in solution. The potential for this standard hydrogen electrode is taken as zero.

When two similar standard hydrogen electrodes are electrically connected to a voltmeter through a salt bridge there will be no net tendency for electrons to flow. There will be a zero potential difference between the two hydrogen electrodes. However, when one of the two hydrogen electrodes is replaced by a dissimilar half cell the voltmeter will record a potential difference which may be 'plus' or 'minus' depending on which way the electron flows. For components of electro-chemical cells involved in electrode reactions, *the standard state is chosen as 1 atmosphere for gases and 1M concentration (activity) for solutions in the electrode compartments.* Metallic electrodes and insoluble compounds do not change in concentration in electrochemical cells, and as along as any amount is present, each insoluble component is also considered to be in standard state. *If a second dissimilar half cell in its standard state is coupled to a standard hydrogen electrode (of zero potential) forming a cell, the measured potential difference of the cell is defined as the standard electrode potential [symbol = $E°$ (volts)] for the second electrode.* It may be noted, however, that the standard hydrogen electrode is rather difficult to manipulate. In practice, electrode potentials on the hydrogen scale are commonly determined indirectly by measuring the electromotive force of a cell formed from the electrode in question and a suitable reference electrode whose

potential is accurately known with respect to the standard hydrogen electrode. Such a subsidiary reference electrode is the saturated calomel electrode. which consists of mercury in contact with solid mercurous chloride and a solution of KCl saturated with the mercurous salt. The calomel electrode with saturated KCl solution has a potential of + 0.2458 volts at 25°C with respect to hydrogen electrode. The half cell reaction is:

$$Hg_2^{2+} + 2e \rightleftharpoons 2Hg$$
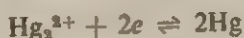
7.4.2. Electrolytic Reactions

An electrolytic cell is a device whereby a non-spontaneous chemical reaction is brought about through the agency of an external source of current. The process occurring within such a cell is called electrolysis. An electrolytic cell is thus the reverse of an electro-chemical cell. A simple but an excellent example is the extraction of metallic sodium by the Down's process. In this process fused sodium chloride is used as the electrolyte. The cell is provided with a circular iron cathode and a centrally placed graphite anode. The cathode is connected to the negative terminal and the anode to the positive terminal of an external source of direct current. The external source maintains a pressure of electrons at the cathode and thus forces the following reactions:

$$NaCl \rightarrow Na^+ + Cl^-$$

at the cathode : $Na^+ + e \rightarrow Na$ (reduction)

at the anode : . $2 Cl^- \rightarrow Cl_2 + 2e$ (oxidation)
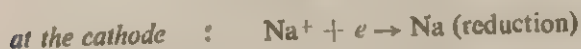
A very useful application of electrolysis is found in commercial electroplating. Let us take the case of copper plating. The material to be copper plated is first cleaned and is then suspended into a bath of aqueous copper sulphate. This material is made the cathode by connecting it to the negative terminal of an external source of current. A strip of pure copper metal dipped into the same solution is connected to the positive terminal. The copper strip thus acts as the anode. The following reactions take place at the two electrodes:

at the cathode : $Cu^{2+} + 2e \rightarrow Cu$ (reduction)

at the anode : $Cu \rightarrow Cu^{2+} + 2e$ (oxidation)
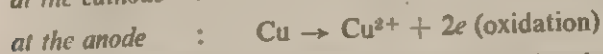
Electrolytic purification of impure copper also involves the above procedure. Plates of impure copper are made anodes while graphite-coated sheets of pure copper act as the cathodes. For silver plating or gold plating the electrolyte consists of a soluble silver salt or gold salt alongwith excess cyanide ion. The argentocyanide or the aurocyanide so formed dissociates to a small extent. As a result the cathode deposit is smooth and adheres well to the surface of the cathode. In the absence of cyanide the cathode deposit is rough and non-adherent. Silver or gold plate acts as the anode. The reactions are:

at the cathode : $[Ag(CN)_2]^- \rightarrow Ag^+ + 2CN^-$; $Ag^+ + e \rightarrow Ag$

at the anode : $Ag \rightarrow Ag^+ + e$; $Ag^+ + 2CN^- \rightarrow [Ag(CN)_2]^-$
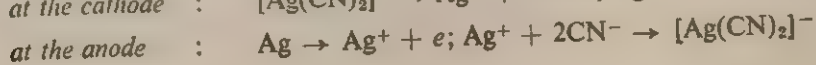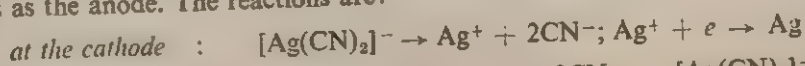
7.4.3. Lead Storage Battery and Nickel Storage Battery

A. Lead Storage Battery : *A lead storage battery* consists of alternate lead plates (acting as anode) and lead plates covered with PbO_2 (acting as cathode). Dilute H_2SO_4 acts as the electrolyte. The following reactions take place when the battery supplies current:

Anode Reaction   : $Pb(s) + SO_4^{2-} \rightarrow PbSO_4(s) + 2e$

Cathode Reaction : $PbO_2(s) + 4H^+ + SO_4^{2-} + 2e \rightarrow PbSO_4(s)$ $2H_2O$

Overall Reaction : $Pb(s) + PbO_2(s) + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4(s) + 2H_2O$
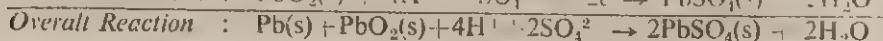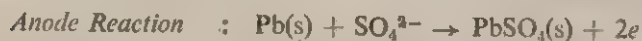
As the battery continues to supply current the concentration of H_2SO_4 as well as the voltage drop. The battery can be brought back to its original condition by passing a direct current through the cell in opposite direction. During charging the battery functions as an electrolytic cell and the overall reaction is reversed:

$$2PbSO_4(s) + 2H_2O \rightarrow Pb(s) + PbO_2(s) + 4H^+ + 2SO_4^{2-}$$
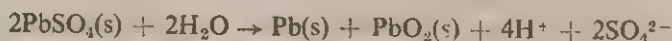
B. Nickel Storage Battery (Edison Cell) : In this cell an iron plate and a rod of Ni_2O_3 are dipped in an aqueous solution of KOH. The iron plate acts as anode and the Ni_2O_3 rod as the cathode during discharge i.e. when the cell functions as an electrochemical cell to supply current. The following reactions take place:

at the anode   : $Fe + 2OH^- \rightarrow Fe(OH)_2 + 2e$

at the cathode : $Ni_2O_3 + 3H_2O + 2e \rightarrow 2Ni(OH)_2 + 2OH^-$

net reaction   : $Fe + Ni_2O_3 + 3H_2O \rightarrow Fe(OH)_2 + 2Ni(OH)_2$
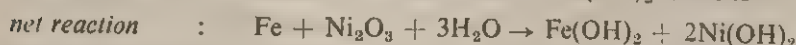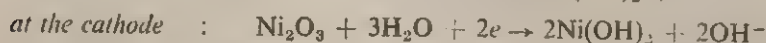
During the course of the above reactions there is no consumption of the electrolyte, KOH. One such cell gives a voltage of 1.35 volts. The battery can be regenerated by reversing the flow of electricity through the cell with an external source of direct current. During such charging reactions the Edison cell acts as an electrolytic cell:

at the anode   : $2Ni(OH)_2 + 2OH^- \rightarrow Ni_2O_3 + 3H_2O + 2e$

at the cathode : $Fe(OH)_2 + 2e \rightarrow Fe + 2OH^-$

net reaction   : $Fe(OH)_2 + 2Ni(OH)_2 \rightarrow Fe + Ni_2O_3 + 3H_2O$
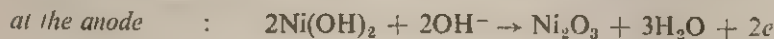
The Ni_2O_3 is obtained by the following reaction:

$$2Ni(OH)_2 + NaOCl \rightarrow Ni_2O_3 + NaCl + 2H_2O$$

7.5. STANDARD ELECTRODE POTENTIALS OF METALS

Considerable confusion has been created by the use of different sign conventions for standard single electrode potentials. According to the international convention the sign of the electrode potential is the same as that of the electrostatic charge on the electrode. Thus the Cd^{2+}/Cd electrode has a potential of -0.403 volts (negative sign), because the tendency is for Cd metal to pass into aqueous

solution as Cd^{2+} ions. thus creating an accumulation of electrons on the electrode surface. The international convention tells us readily which terminal of a potentiometer a particular electrode has to be connected to. Thus if we make a cell from Cd electrode and a hydrogen electrode (alongwith a salt bridge) it is the Cd electrode that will have to be connected to the negative terminal of the potentiometer.

Some American texts still use an opposite convention of writing the electrode reaction as $Cd \rightleftharpoons Cd^{2+} + 2e$ $(E = + 0.403$ volts) instead of the international convention $Cd^{2+} + 2e \rightleftharpoons Cd$ $(E^\circ = -0.403$ volts). According to the international convention standard electrode potentials are, in fact, standard reduction poten-

Table 7.1. Standard Electrode Potentials (25°C)

Electrode reaction	E° (volts)
Pt^2 $+ 2e \rightleftharpoons Pt$	$+ 1.200$
Pd^{2+} $+ 2e \rightleftharpoons Pd$	$+ 0.987$
Ag^+ $+ e \rightleftharpoons Ag$	$+ 0.799$
Hg^{2+} $+ 2e \rightleftharpoons Hg$	$+ 0.789$
Cu^{2+} $+ 2e \rightleftharpoons Cu$	$+ 0.337$
$2H^+$ $+ 2e \rightleftharpoons H_2$	0.000
Pb^{2+} $+ 2e \rightleftharpoons Pb$	$- 0.126$
Sn^{2+} $+ 2e \rightleftharpoons Sn$	$- 0.136$
Ni^{2+} $+ 2e \rightleftharpoons Ni$	$- 0.25$
Co^{2+} $+ 2e \rightleftharpoons Co$	$- 0.277$
Cd^{2+} $+ 2e \rightleftharpoons Cd$	$- 0.403$
Fe^{3+} $+ 2e \rightleftharpoons Fe$	$- 0.440$
Zn^{2+} $+ 2e \rightleftharpoons Zn$	$- 0.763$
Mn^{2+} $+ 2e \rightleftharpoons Mn$	$- 1.18$
Al^{3+} $+ 3e \rightleftharpoons Al$	$- 1.66$
Be^{2+} $+ 2e \rightleftharpoons Be$	$- 1.85$
Mg^{2+} $+ 2e \rightleftharpoons Mg$	$- 2.37$
Na^+ $+ e \rightleftharpoons Na$	$- 2.714$
Ca^{2+} $+ 2e \rightleftharpoons Ca$	$- 2.87$
Sr^{2+} $+ 2e \rightleftharpoons Sr$	$- 2.89$
Ba^{2+} $+ 2e \rightleftharpoons Ba$	$- 2.90$
K^+ $+ e \rightleftharpoons K$	$- 2.925$
Li^+ $+ e \rightleftharpoons Li$	$- 3.045$

Left margin labels: oxidising strength of the metal ions increases; reduction of the metal ions to metals becomes easy

Right margin labels: reducing strength of the metals increases; reduction of the metal ions to metals becomes more difficult

tials. On the contrary, electrode potentials according to American convention are really standard oxidation potentials.

When metals are arranged in the order of their standard electrode potentials, we have the electrochemical series of the metals (Table 7.1). The potential values are with respect to the hydrogen electrode as the reference. The convention used in writing the electrode reaction is:

$$M^{n+} + ne \rightleftharpoons M$$

A positive potential value means the metal ion has a tendency to be reduced rather than the metal to be oxidised to the metal ion. The more negative the value of the potential, the greater is the tendency of the metal to pass into ions, that is, the greater is its ability to serve as a reducing agent. A metal with a higher negative value of its potential will displace any other metal with a less negative (or positive) value of the potential, from a solution of its ions.

The alkali metals have the most negative potentials. They are thus the best reducing agents known. Consequently the alkali ions are the most difficultly reducible ones. In a periodic group normally standard potentials become more negative with increasing atomic number. This is because with increasing atomic number in a group the valence electrons are placed farther and farther out from the nucleus and are therefore readily lost.

7.6. OXIDATION-REDUCTION POTENTIALS

In metal electrode systems the metal ion behaves as the oxidant and the metal as the reductant. The metal and its own ions constitute the oxidation-reduction couple. An inert platinum electrode dipped into an aqueous solution containing ions of one and the same metal in two oxidation states also constitutes an oxidation-reduction couple. Thus a platinum electrode dipped into a solution containing Fe^{2+} and Fe^{3+} assumes a definite potential, which is indicative of the position of the equilibrium. If the system tends to show reducing properties, then electrons will be released to platinum at the cost of the reaction $Fe^{2+} \rightarrow Fe^{3+} + e$. On the other hand when the system tends to show oxidising properties it will extract electrons from platinum and the reaction $Fe^{3+} + e \rightarrow Fe^{2+}$ will occur. The magnitude of the potential will thus be a measure of the oxidising or reducing character of the system. Once again standard potentials of such systems can be obtained from measurements relative to a standard hydrogen electrode, under standard experimental conditions. The oxidant (say Fe^{3+}) and the reductant (Fe^{2+}) are maintained at 1 M concentration, correctly unit activity.

A relation connecting the observed potential with the standard potential and the concentration of the oxidised and reduced form of the couple will now be developed.

The degree of spontaneity of a reaction (when all the reactants and products are at standard state) is indicated by the change in free energy of the reaction. The free energy change reflects the driving force of a reaction, and expectedly there is a connection between free energy change and the equilibrium constant of the reaction, expressed as:

$$\triangle G° = -RT \ln K = -2.303 \; RT \log K$$

A spontaneous reaction is characterised by a negative free energy change. The free energy change of a reaction

$$aA + bB \rightleftharpoons lL + mM$$

is given by $\triangle G = \triangle G° + RT \ln \dfrac{a_L^l \, a_M^m}{a_A^a \, a_B^b}$

where a's represent the activities of the different species. It follows that when all the species are at standard state, that is, unit activity $\Delta G = \Delta G^0$. Now in an electrochemical cell of e.m.f. E,

$$\Delta G = -nFE$$

where ΔG is the free energy change in calories, n is the number of moles of electrons transferred in the reaction, F is the Faraday (96,500 coulombs/mole of electron $= 23,060$ cal/volt) and E is the voltage. The quantity nFE represents the electrical work which is obtainable from the cell. At standard state,

$$\Delta G° = -nFE°$$

where E is the standard potential of the cell. Then we have

$$-nFE = -nFE° + RT \ln \frac{a_L^l\ a_M^m}{a_A^a\ a_B^b}$$

so that

$$E = E° - \frac{RT}{nF} \ln \frac{a_L^l\ a_M^m}{a_A^a\ a_B^b}$$

In these reactions n may be taken rather loosely as the number of electrons involved in the cell reaction. Applying the above considerations to a half cell reaction, the electrode potential may be deduced as follows. An electrode reaction may be written according to international convention:

$$\text{oxidant} + ne \rightleftharpoons \text{reductant}$$

Then we have,

$$E = E° - \frac{RT}{nF} \ln \frac{a_{Red}}{a_{Ox}} = E° + \frac{RT}{nF} \ln \frac{a_{Ox}}{a_{Red}}$$

where E is the observed potential of the redox electrode at temp. T, relative to the standard hydrogen electrode. $E°$ is the standard potential, n is the number of electrons gained by the oxidant and a_{Ox} and a_{Red} are the activities of the appropriate species. R is the gas constant (1.9872 cal/degree/mole or 8.31 volt-coulomb) and F is the Faraday. For our purposes activities may be replaced by concentrations so that

$$E = E° + \frac{RT}{nF} \ln \frac{C_{Ox}}{C_{Red}} = E° + \frac{0.0591}{n} \log \frac{[Ox]}{[Red]}$$

at 25°C. It follows that when the concentrations of the oxidant [Ox] and of the reductant [Red] are equal, E becomes equal to $E°$. Some standard oxidation reduction potentials are given in Table 7.2 at 25°C.

At this point it is necessary to elaborate on two current practices with regard to the sign of oxidation-reduction potentials. The international convention given in Table 7.2 are really standard reduction potentials. However if we write the oxidation-reduction reaction according to the American convention:

$$\text{Reductant} \rightleftharpoons \text{Oxidant} + ne$$

then the reaction points to oxidation so that the standard potentials will be really oxidation potentials, taking the following form:

$$E = E° - \frac{RT}{nF} \ln \frac{[Ox]}{[Red]} = E° - \frac{0.0591}{n} \log \frac{[Ox]}{[Red]}$$

where $E°$ is the standard oxidation potential. Writing a common example the two conventions are:

International : $Fe^{3+} + e \rightleftharpoons Fe^{2+}$; $E° = + 0.77$ volts
American   : $Fe^{3+} \rightleftharpoons Fe^{2+} + e$; $E° = - 0.77$ volts
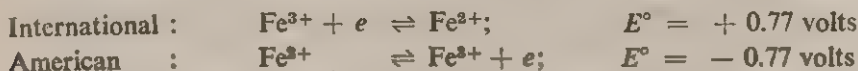
According to the international convention the more positive the $E°$ value (the higher the standard reduction potential) is, the greater is the tendency of the oxidant to pass to the reductant, that is, a stronger oxidant has a greater positive $E°$ value. The more negative the value of $E°$ is, the weaker is the oxidant or in other words the reductant will tend to be oxidised. On the contrary according to the American convention the more positive the $E°$ value (the higher the standard oxidation potential) is, the greater is the tendency for the reductant to pass on to the oxidant form. Also the more negative the $E°$ value is, the greater will be the tendency for the oxidant to pass on to the reductant. Let us take the following couples:

Couple	International Convention	Couple	American Convention
$Ce^{4+} + e \rightleftharpoons Ce^{3+}$;	$E° = 1.44$ volts	$Ce^{3+} \rightleftharpoons Ce^{4+} + e$;	$E° = -1.44$ volts
$Fe^{3+} + e \rightleftharpoons Fe^{3+}$;	$E° = 0.77$ volts	$Fe^{3+} \rightleftharpoons Fe^{3+} + e$;	$E° = -0.77$ volts
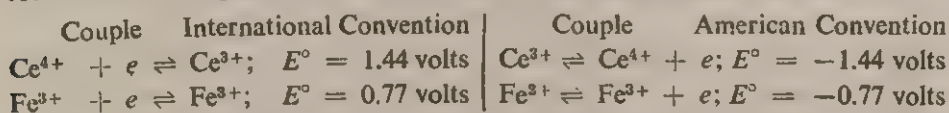
According to the international convention Ce^{4+}/Ce^{3+} couple having a more positive $E°$ value than the Fe^{3+}/Fe^{2+} couple means that Ce^{4+} is a stronger oxidant than Fe^{3+}. Therefore Ce^{4+} will oxdise Fe^{2+} ion. But the American convention shows that Ce^{3+}/Ce^{4+} couple has a more negative $E°$ value than the Fe^{2+}/Fe^{3+} couple meaning thereby that Ce^{3+} is a weaker reductant than Fe^{2+} so that Fe^{2+} will reduce Ce^{4+} to Ce^{3+}. So whichever convention we follow correctly we come to the same conclusion. However we will use the international convention in our subsequent discussions.

Note that the most powerful oxidising agents are the left hand ions at the top area of Table 7.2. Thus F_2, $S_2O_8^{--}$, MnO_4^- are the most powerful oxidants with high positive potential values for their couples, whereas the corresponding reduced forms are the weakest reducing agents. *The oxidant of a couple with a more positive standard potential value will, in general, oxidise the reductant of a couple with a less positive (or negative) standard potential. Conversely the reductant of a couple with less positive standard potential will, in general, reduce the oxidant of the couple with more positive standard potential.*

7.7. FORMAL POTENTIALS

Standard potentials $E°$ are evaluated with respect to activity and with all ions expressed in simple ion forms as shown in Table 7.2. In practice the solution may be quite concentrated making activity and concentration unequal and further may contain the ions not in their simple form but in the form of complex ions.

Under such conditions the activities of the species are smaller than their concentrations. The actual species involved may often differ from those to which the standard potentials refer. To recognise such situations, standard redox potentials are replaced by the more practical and useful formal potentials. The formal potential is the experimentally determined potential of a solution having equal formal

Table 7.2. Standard Oxidation-Reduction Potentials (25°C)

Half reaction	E (volts)
$F_2 + 2e \rightleftharpoons 2F^-$	+ 2.65
$S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{2-}$	+ 2.01
$Co^{3+} + e \rightleftharpoons Co^{2+}$	+ 1.82
$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 + 2H_2O$	+ 1.69
$Ce^{4+} + e \rightleftharpoons Ce^{3+}$	+ 1.44
$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$	+ 1.52
$Cl_2 + 2e \rightleftharpoons 2Cl^-$	+ 1.36
$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O$	+ 1.33
$Br_2 + 2e \rightleftharpoons 2Br^-$	+ 1.07
$2Hg^{2+} + 2e \rightleftharpoons Hg_2^{2+}$	+ 0.92
$Cu^{2+} + I^- + e \rightleftharpoons CuI$	+ 0.86
$O_2 + 2H_2O + 4e \rightleftharpoons 4OH^- (1.0 \times 10^{-7}M)$	+ 0.82
$Hg_2^{2+} + 2e \rightleftharpoons 2Hg$	+ 0.79
$Fe^{3+} + e \rightleftharpoons Fe^{2+}$	+ 0.77
$Cu^{2+} + Cl^- + e + CuCl$	+ 0.54
$I_2 + 2e \rightleftharpoons 2I^-$	+ 0.54
$[Fe(CN)_6]^{3-} + e \rightleftharpoons [Fe(CN)_6]^{4-}$	+ 0.36
$Cu^{2+} + e \rightleftharpoons Cu^+$	+ 0.15
$Sn^{4+} \rightleftharpoons 2e \rightleftharpoons Sn^{2+}$	+ 0.15
$2H^+ + 2e \rightleftharpoons H_2$	0.00
$V^{3+} + e \rightleftharpoons V^{2+}$	− 0.26
$2H^+(1.0 \times 10^{-7}M) + 2e \rightleftharpoons H_2$	− 0.41
$Cr^{3+} + e \rightleftharpoons Cr^{2+}$	− 0.41
$Fe(OH)_3 + e \rightleftharpoons Fe(OH)_2 + OH^-$	− 0.56
$AsO_4^{3-} + 3H_2O + 2e \rightleftharpoons H_2AsO_3^- + 4OH^-$	− 0.67

oxidising strength increases (left margin, upward)

reducing strength increases (right margin, upward)

concentrations of the oxidised and reduced species in presence of any other substance that might accompany the oxidised and reduced species under the actual reaction conditions. Formal potentials cover the effects of the concentrations of the species, pH of the solution, any complexation in solution etc. Formal concentrations or formality F is the number of formula weights of a substance per litre of the solution. Note for example, that the standard potential of $Hg_2^{2+} + 2e \rightleftharpoons 2Hg$ is + 0.79 volts whereas the formal potential of the calomel electrode in saturated KCl is 0.2458 volts. The ferric-ferrous system has $E° = + 0.77$

volt. But the formal potentials in different acid media are: $+$ 0.73 volt in 1 M $HClO_4$, $+$ 0.70 volts in 1M HCl, $+$ 0.68 volt in 1M H_2SO_4 and $+$ 0.61 volt in 0.5M H_3PO_4 $+$ 1M H_2SO_4. Thus in perchloric acid the formal potential is closest to $E°$ and in H_3PO_4 $+$ H_2SO_4 medium a substantially lower value of the formal potential is obtained due to complex formation between ferric ions and phosphate and sulphate ions. It should be noted that formal potentials are considerably dependent on factors like pH, complex formation and solubility of the species involved.

7.8. APPLICATIONS OF OXIDATION-REDUCTION POTENTIALS

7.8.1. Prediction of Reactions : Consider the standard electrode potentials of the following couples:

$$Cu^{2+} + 2e \rightleftharpoons Cu; \qquad E° = + 0.337 \text{ volts}$$
$$Ag^+ + e \rightleftharpoons Ag; \qquad E° = + 0.799 \text{ volts}$$
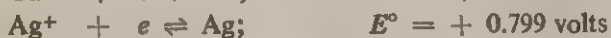
The more negative (that is the less positive) the potential of the couple, the more effective the metal is as a reducing agent. Since the copper (II)—copper couple has a less positive potential copper will serve as a better reducing agent. Copper metal will therefore pass into solution with greater ease than silver metal. Therefore if a copper wire is dipped into an aqueous solution of silver nitrate, copper will pass into solution as Cu^{2+} leaving electrons on its surface. These electrons will react with Ag^+ ions, which will be reduced to silver. Effectively there will be a deposit of silver on the copper wire and the colourless aqueous solution will assume a blue colour due to copper (II) ions. On the contrary when a silver wire is dipped into a cupric solution there will be no reaction. Similarly, when a zinc rod is placed in a solution containing copper (II) ions, there is a deposit of metallic copper on the zinc rod. On the other hand, if copper rod is immersed in a solution of zinc ion, no reaction occurs. The student should convince him of the fact that elements having negative potentials can liberate H_2 from H^+ ions (acids) whereas elements with positive potentials cannot.

7.8.2. Calculation of Cell Potentials : The data furnished in the Tables of electrode potentials can be utilised in calculating the electromotive force of a cell. Cell potentials can be calculated by adding algebraically the standard electrode potentials of the electrodes in the cell. Thus the cell potential of the cell can be

$$Zn \mid Zn^{2+} \parallel Ag^+ \mid Ag$$

derived by adding algebraically the two single electrode potentials $(-(-0.763) + 0.799 = 1.562$ volts). Since the zinc side has a negative potential there will be release of zinc ions in solution. On the other electrode silver ions from solution will be deposited on the silver electrode surface. Electrons will flow from the zinc electrode to the silver electrode. A cell potential diagram is shown in Fig. 7.3. The cell potential of the cell

$$Zn \mid Zn^{2+} \parallel Fe^{2+} \mid Fe$$

is found to be $[-(-0.763) - (0.44)] = 0.323$ volts.

It should be pointed out here that in order to make atom balance or electron balance between two half cell reactions we are free to multiply any of the half cell equations by a coefficient. However we cannot multiply the half cell potential by any coefficient. The $E°$ remains unaffected. This is because potential values measure losses of some electron per atom or ion and remains independent of the total number of atoms or ions of the variety.

7.8.3. The Utility of Formal Potentials : The use of standard potentials may lead to erroneous conclusion. For example the standard potentials of ferrocyanide-ferricyanide couple and iodide-iodine couple are:

$$[Fe(CN)_6]^{3-} + e \rightleftharpoons [Fe(CN)_6]^{4-}; \quad E° = + 0.36 \text{ volts}$$
$$I_2 + 2e \rightleftharpoons 2I^- \qquad ; \quad E° = + 0.54 \text{ volts}$$
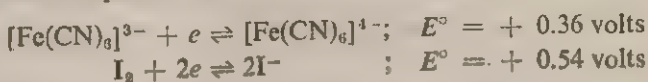
Since the iodine-iodide couple has a greater positive potential than the ferricyanide-ferrocyanide couple. the iodide ion appears to be an inferior reducing agent than the ferrocyanide ion. This means that iodine is a better oxidant than ferricyanide ion. Therefore it would be expected that iodine would oxidise ferrocyanide to ferricyanide ion:

$$2[Fe(CN)_6]^{4-} + I_2 \rightarrow 2[Fe(CN)_6]^{3-} + 2I^-$$

In reality, however, it is the ferricyanide ion that oxidises iodide ion to free iodine in acid medium. This apparent violation of the concept of standard potential can be explained in terms of formal potentials. In solutions of low pH($1M$ H^+), ferrocyanide and ferricyanide ions combine with one or more hydrogen ions to form hydroferrocyanic and hydroferricyanic acid species. Since increasing charge on a metal ion increases its acid character, the reactivity of ferrocyanide ion (Fe^{2+}) with H^+ ion is more than the reactivity of ferricyanide ion (Fe^{3+}) with H^+. Ferrocyanide is a stronger base than ferricyanide and hence the enhanced activity. Thus the concentration of ferrocyanide is appreciably diminished in acid solution, and the potential is raised from $+ 0.36$ volts in neutral solution to $+ 0.71$ volts in $1M$ HCl, H_2SO_4 or $HClO_4$. The formal potential is now above that of iodide-iodine couple, and oxidation of iodide to iodine by ferricyanide becomes a reality.

FIG. 7.3 Cell potential diagram

Comparison of the potential values of iodine-iodide couple ($+ 0.54$ volts) with that of the cupric-cuprous couple ($+ 0.15$ volts) would also indicate that cupric ion will not oxidise iodide ion to iodine. Since iodometric estimation of copper (II) involves cuprous iodide, which is only sparingly soluble, the couple

$$Cu^{2+} + I^- + e \rightleftharpoons CuI \ (E° = + 0.86 \text{ volts})$$
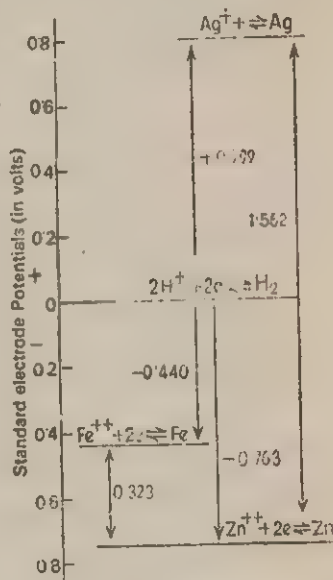
need be considered rather than the couple

$$Cu^{2+} + e \rightleftharpoons Cu^+ \ (E^\circ = + 0.15 \text{ volts})$$

7.8.4. Equilibrium Constants, Oxidation-Reduction Titration Curves and Choice of Indicators : We have earlier shown that a study of the standard potentials of different couples helps us in predicting which reactions are possible and which ones are not. The standard potentials also help us to calculate the equilibrium constant of a redox reaction, and therefrom to decide if a particular reaction will proceed to completion. Let us take a simple example of oxidation of ferrous ion to ferric ion by ceric ions in the presence of dilute sulphuric acid. The reaction is:

$$Ce^{4+} + Fe^{2+} \rightleftharpoons Ce^{3+} + Fe^{3+}$$

Equilibrium constant, K, is given by

$$K = \frac{[Ce^{3+}] \, [Fe^{3+}]}{[Ce^{4+}] \, [Fe^{2+}]}$$

The above reaction involves two systems, the ferric-ferrous ion electrode (1) and the ceric-cerous electrode (2). Then taking the E° values from Table 7.2 we have:

$$E_1 = E_1^\circ + 0.0591 \log \frac{[Fe^{3+}]}{[Fe^{2+}]} = 0.77 + 0.0591 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$E_2 = E_2^\circ + 0.0591 \log \frac{[Ce^{4+}]}{[Ce^{3+}]} = 1.44 + 0.0591 \log \frac{[Ce^{4+}]}{[Ce^{3+}]}$$

Then $\qquad \log K = \frac{1}{0.0591} [E_1 - 0.77 - E_2 + 1.44]$

when equilibrium is established there is no motive for further reaction, the e.m.f. of the cell will be zero, and the potentials E_1 and E_2 of the two electrodes will be equal. Then

$$\log K = 11.3; \ K = 2 \times 10^{11}$$

Since the equilibrium constant of the reaction is very high the reaction will proceed to completion.

We can also derive the equilibrium constant in an alternative way by making use of the free energy change in the reaction. The individual half cell reactions are:

$$Ce^{4+} + e \rightleftharpoons Ce^{3+} \quad ; \qquad E_2^\circ = 1.44 \text{ volts}$$

$$Fe^{3+} + e \rightleftharpoons Fe^{2+} \quad ; \qquad E_1^\circ = 0.77 \text{ volts}$$

so that the overall reaction is:

$$Ce^{4+} + Fe^{2+} \rightleftharpoons Ce^{3+} + Fe^{3+}; \ E^\circ = 0.67 \text{ volts}$$

Then the standard free energy change of the reaction is given by

$$\triangle G^\circ = -FE^\circ \text{ with } E^\circ = 0.67 \text{ volts, remembering } n = 1;$$

since $\triangle G^\circ = -RT \ln K = -nFE^\circ$

$$E = \frac{RT}{nF} \ln K = \frac{0.0591}{n} \log K \text{ and } \log K = \frac{nE^\circ}{0.0591}$$

In the above case $n = 1$ so that $\log K = \dfrac{1 \times 0.67}{0.0591} = 11.3$ and $K = 2 \times 10^{11}$

We take one other example of common analytical importance.

$$Sn^{4+} + 2e \rightleftharpoons Sn^{2+} \quad ; \qquad E^\circ = 0.15 \text{ volts}$$

$$Fe^{3+} + e \rightleftharpoons Fe^{2+} \quad ; \qquad E^\circ = 0.77 \text{ volts}$$

The standard free energy change of the overall reaction

$$Sn^{2+} + 2Fe^{3+} \rightleftharpoons 2Fe^{2+} + Sn^{4+}; E^\circ = 0.62 \text{ volts}$$
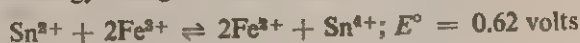
would be $\quad \triangle G^\circ = -nFE^\circ = -2FE^\circ \ (n = 2)$

Then $\qquad\qquad\qquad \log K = \dfrac{2 \times 0.62}{0.0591} = 21$

$$K = 10^{21}$$

The reduction of ferric ions by stannous ion must threfore proceed to completion. In general, a couple of higher positive potential will oxidise a couple of lower potential. When the potentials of the individual couples are similar, the value of K will be small and the reaction will remain incomplete. In such cases, the equilibrium may be shifted by insolubility of the product or through complexation.

The standard potential data can also be used to determine the theoretical shape of a titration curve involving oxidation of ferrous iron by ceric ion. On addition of ceric ion oxidation will occur and consequently the ferric-ferrous ratio will continue to increase. The electrode potential can be calculated given the knowledge of E° and the $[Fe^{3+}]/[Fe^{2+}]$ ratio. If we start with 100 ml of 0.1 N Fe^{2+} and titrate this with 0.1 N Ce^{4+} solution we have:

Volume of Ce^{4+} solution;	$[Fe^{3+}]/[Fe^{2+}]$	$E = E^\circ + 0.0591 \log [Fe^{3+}]/[Fe^{2+}]$	
10 ml	10/90	$0.77 + 0.0591 \log 10/90$	$= 0.69$ volts
20 ,,	20/80	$0.77 + 0.0591 \log 20/80$	$= 0.73$
50 ,,	50/50	$0.77 + 0.0591 \log 50/50$	$= 0.77$
90 ,,	90/10	$0.77 + 0.0591 \log 90/10$	$= 0.83$
99.9 ml	99.9/0.1	$0.77 + 0.0591 \log 99.9/01.$	$= 0.95$
100.0 ,,	.—	$(0.77 + 1.44)/2$	$= 1.10$
100.1 ,,	—	$1.44 + 0.0591 \log 0.1/100$	$= 1.26*$
101 ,,	—	$1.44 + 0.0591 \log 1/100$	$= 1.32*$
110 ,,	—	$1.44 + 0.0591 \log 10/100$	$= 1.38*$

In the calculation of the electrode potential prior to the equivalence point we need to consider only the $[Fe^{2+}]/[Fe^{2+}]$ since there will be no appreciable $[Ce^{4+}]$ ion in solution. At the equivalence point calculation of the potential involves some approximations and the potential is given by one-half of the sum of the two single electrode potentials. After the equivalence point addition of ceric ion simply increases the ceric-cerous ratio and the potential calculation has to take into account this ratio along with the standard potential, 1.44 volts. The ferric-ferrous

---

* $E = E^\circ + 0.0591 \log [Ce^{4+}]/[Ce^{3+}]$

ratio need not be considered since there is practically no ferrous ion left after the equivalence point. If these theoretical potential values are plotted against volume of ceric solution the curve will be the one shown in Fig. 7.4. Potential slowly rises, then suddenly shows a steep rise at the equivalence point and then rises slowly again. The steep rise is connected with a relatively large change in the ferric-ferrous ratio at the equivalence point.

Fig 7.4. Calculated potentiometric titration curve of 100 ml of 0.1 N Fe^{2+} with 0.1 N Ce^{4+} in dilute H_2SO_4

The choice of an indicator in such a titration is dictated by the oxidation potential of oxidised-reduced form of the indicator. Thus [Fe (phenanthroline)$_3$]$^{3+}$/[Fe (phenanthroline)$_3$]$^{2+}$ couple has an oxidation potential of 1.14 volt and will serve as a suitable indicator in the titration of ferrous ion by ceric ion in dilute sulphuric acid medium. All the ferrous ion is first oxidised by the ceric ion with a potential of 1.1 volt at the equivalence point. The next drop of the ceric solution will oxidise the indicator and the visual endpoint of the titration will be marked by a sudden change of colour from red to blue.

Another common example may be discussed profitably. Ferrous ion is quantitatively titrated by potassium dichromate in acid medium using diphenylamine as an indicator. Diphenylamine (I) is first oxidised to diphenylbenzidine (II), which is the effective indicator and may be further oxidised to diphenylbenzidine violet (III) The oxidation-reduction potentials of the three couples are:

Fe^{3+}/Fe^{2+}, 0.77; $Cr_2O_7^{2-} + 14H^+ + 6e/2Cr^{3+} + 7H_2O$, 1.33; diphenylbenzidine violet/diphenylbenzidine, 0.76 volts. It is immediately apparent that dichromate will simultaneously oxidise both the ferrous ion and the indicator. It is essential therefore that the potential of the Fe^{3+}/Fe^{2+} system be lowered in order that diphenylamine can be used as an indicator. Phosphoric acid is therefore added prior to the start of the titration. The phosphoric acid forms a complex with ferric ion [Fe(HPO$_4$)]$^+$ and thus substantially lowers the potential. The
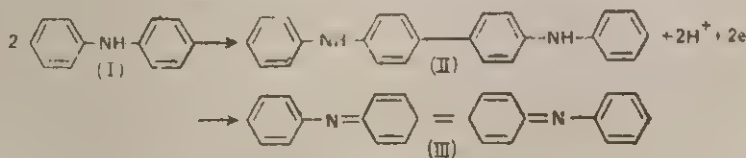
formal potential of the ferric-ferrous system in 0.5M H_3PO_4 + 2N H_2SO_4 is 0.61 volts. After all the ferrous is oxidised to the ferric state, dichromate oxidises the indicator. The end point is marked by a sudden change of colour from pale green to violet. However if N-phenylanthranilic acid (oxidised form, purple red; reduced

form, colourless) of redox potential 1.08 volts in $1N$ H_2SO_4 medium is used as indicator, the titration may be done without the use of phosphoric acid. For a dependable colour change at the end point the $E°$ value of the indicator should be at least 0.2-0.3 volts more positive than the standard formal potential of the system under titration.

7.8.5. Influence of Precipitation, Complex Formation and pH and Redox Potentials:
Standard potentials refer to the reductant and the oxidant of a redox couple being present at standard condition i.e., 1 M solution and 1 atmosphere pressure. In reality when chemical reactions are progressing hardly do we encounter standard conditions. In the event of precipitation or complex formation concentration of one of the reactants or products is being lowered. In such cases $E°$ values no longer hold; instead we get formal potentials. Because of precipitation or complexation an oxidant may be made to appear stronger (or weaker) or a reductant may be made stronger (or weaker). As a result some reactions which may appear forbidden from a consideration of standard potentials alone may turn out to be feasible in practice. In some redox reactions H^+ is also a participant and concentration of H^+ ($[H^+]$) appears in the equation of oxidation - reduction potential. Addition or removal of H via change of pH of the solution will eventually influence the potential value and consequently will influence the course and nature of the redox reaction.

It is a common-place knowledge that cupric ion can be estimated iodometrically by titrating the iodine liberated from iodide ion:

$$2Cu^{2+} + 4I^- = 2CuI \downarrow + I_2$$
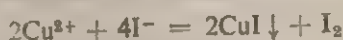
A consideration of the potentials of the cupric-cuprous couple and of the iodine-iodide couple:

$$Cu^{2+} + e \rightleftharpoons Cu^+; \qquad E° = +0.15 \text{ volts}$$
$$I_2 + 2e \rightleftharpoons 2I^-; \qquad E° = +0.54 \text{ volts}$$
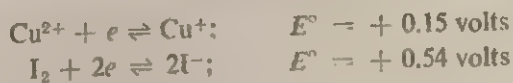
would indicate a reverse reaction:

$$2Cu^+ + I_2 = 2Cu^{2+} + 2I^-$$

The anomaly can be explained by taking into consideration the sparing solubility of cuprous iodide. Assuming the iodide concentration as 0.1 M and taking the solubility product of CuI as 10^{-12} we have:

$$K_{SP} = [Cu^+].[I^-]: [Cu^+] = \frac{10^{-12}}{10^{-1}} = 10^{-11}M$$

The potential of the Cu^{2+}/Cu^+ couple then becomes:

$$E = 0.15 + \frac{0.0591}{1} \log \frac{[Cu^{2+}]}{10^{-11}}$$
$$= 0.799 + 0.0591 \log [Cu^{2+}]$$

Since 0.799 is larger than the $E°$ of the I_2/I^- couple it follows that the preferred reaction is:

$$2Cu^{2+} + 4I^- = 2CuI \downarrow + I_2$$

Potassium permanganate is a strong oxidant and is often used in the estimation of ferrous iron. The relevant E° values are:

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O; \quad E^\circ = \; : \; 1.52 \text{ volts}$$
$$Fe^{3+} + e \rightleftharpoons Fe^{2+} \qquad : \; E^\circ = + 0.77 \text{ volts}$$
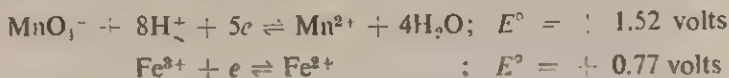
If the acidity of the solution is maintained by the use of H_2SO_4 no complicating side reactions occur. On the contrary if HCl is used complications arise due to oxidation of the chloride ion to chlorine:

$$2MnO_4^- + 10Cl^- + 16H^+ = 2Mn^{2+} + 5Cl_2 + 8H_2O$$
$$Cl_2 + 2e \rightleftharpoons 2Cl^-; \quad E^\circ = + 1.36 \text{ volts.}$$
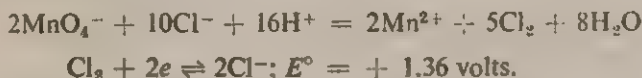
The chlorine formed in the side reaction, however, is expected to oxidise the ferrous ion immediately to ferric. Unfortunately chlorine has a low solubility in aqueous acidic solution and much of it is lost to air. In order to obviate this side effect in HCl medium Zimmermann-Reinhardt solution (the so called preventive solution) is added to the ferrous solution prior to the titration. The preventive solution contains manganous sulphate, sulphuric acid and phosphoric acid. The redox potential of MnO_4^-/Mn^{2+} couple is given by:

$$E = E^\circ + \frac{0.0591}{5} \log \frac{[MnO_4^-] \, [H^+]^8}{[Mn^{2+}]}$$

$$= 1.52 + \frac{0.0591}{5} \log \frac{[MnO_4^-]}{[Mn^{2+}]} + \frac{0.0591}{5} \log [H^+]^8$$

Under standard conditions, the concentrations of both MnO_4^- and Mn^{2+} are 1 M, their ratio being 1. On the addition of the preventive solution there is already much Mn^{2+} present in the ferrous solution so that the ratio $[MnO_4^-]/[Mn^{2+}]$ is considerably lower than 1. The redox potential will, then, be substantially lower than the E° value of $+ 1.52$ volts. Thus permanganate is made a weaker oxidant. Again presence of phosphoric acid complexes iron (III) as colourless $[Fe(HPO_4)]^+$, effectively lowering the concentration of free Fe^{3+} in solution. The redox potential of Fe^{3+}/Fe^{2+} couple is also reduced so that ferrous iron turns out to be a stronger reducing agent than it appears from its E° value. In summary the preventive solution does not allow $KMnO_4$ to oxidise HCl. It may be mentioned, however, that some Mn(III) is produced which quantitatively oxidises Fe^{2+} to Fe^{3+}.

The Hg^{2+}/Hg_2^{2+} couple has E° of $+ 0.92$ volts. Fe^{2+}, under standard condition reduces Hg^{2+} to Hg_2^{2+}. In the presence of thiocyanate ion Hg^{2+} is strongly complexed as $[Hg(SCN)_4]^{2-}$ whereby the concentration of free Hg^{2+} in solution is lowered. If the ratio is lowered from 1 to 10^{-3} M the E will change from E° 0.92 volts to $+0.743$ volts. Thus Hg_2^{2+} becomes a stronger reductant than Fe^{3+}. In fact Hg_2^{2+} can be detected by its ability to force reduction of Fe^{3+} to Fe^{2+} in the presence of thocyanate ion.

That pH of a solution is very important in deciding the direction and course of a redox reaction (where H^+ is a participant) is nicely demonstrated by the oxidation of iodide ion in acid medium by AsO_4^{3-} and the oxidation of

AsO_3^{3-} by iodine in neutral or alkaline medium. The relevant oxidation-reduction potentials are:

$$AsO_4^{3-} + 2H^+ + 2e \rightleftharpoons AsO_3^{3-} + H_2O; \qquad E^\circ = + 0.56 \text{ volts}$$

$$I_2 + 2e \rightleftharpoons 2I^- \qquad ; \qquad E^\circ = + 0.54 \text{ volts}$$
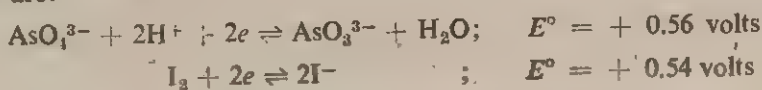
The following reaction takes place when the medium is sufficiently acidic:

$$AsO_4^{3-} + 2I^- + 2H^+ = AsO_3^{3-} + I_2 + H_2O$$
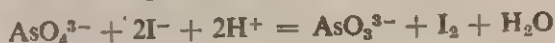
If the solution is brought to a pH 8 by the addition of $NaHCO_3$ the $[H^+]$ becomes 10^{-8}. This lowering of $[H^+]$ from standard value of 1 to 10^{-8} now entirely changes the very direction of the redox reaction. The E of the AsO_4^{3-}/AsO_3^{3-} is given by:

$$E = 0.56 + \frac{0.059}{2} \log \frac{[AsO_4^{2-}] \ [10^{-8}]^2}{[AsO_3^{3-}]}$$

$$= 0.088 + \frac{0.059}{2} \log \frac{[AsO_3^{3-}]}{[AsO_4^{3-}]}$$

It is immediately apparent that the potential value of the AsO_4^{3-}/AsO_3^{3-} system at pH 8 drops far below that of the $I_2/2I^-$ system, thus making AsO_4^{3-} a far weaker oxidant than iodine. Therefore the reverse reaction now takes place:

$$AsO_3^{3-} + I_2 + H_2O = AsO_4^{3-} + 2H^+ + 2I^-$$
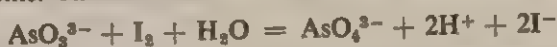
It is a common practice to determine copper (II) iodometrically in a mixture of copper (II) and iron (III) by prior masking of the iron (III) by excess fluoride ion. On the addition of excess fluoride ions iron (III) is converted to a strong complex $[FeF_6]^{3-}$ and as a result the redox potential of the Fe^{3+}/Fe^{2+} is substantially reduced from the value of 0.77 volts so that iron (III) can no longer oxidise any iodide ion to iodine. But copper (II) does not form such a fluoro complex so that it can still liberate iodine from iodide ion.

7.9. EQUIVALENT WEIGHT OF OXIDANT AND REDUCTANT

In an elementary way the equivalent weight of oxidants can be calculated from the number of oxygen atoms that may be supposed to be released from some hypothetical equations such as:

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$
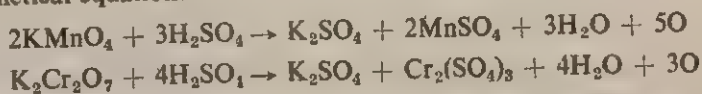
The equivalent weights of $KMnO_4$ and $K_2Cr_2O_7$ are just one-fifth, and one-sixth of the respective formula weights. On the other hand the equivalent weights of reducing agents can be determined from the way they would react with oxygen:

$$2Na_2S_2O_3 + O + H_2O \rightarrow Na_2S_4O_6 + 2NaOH$$

This reaction shows that the equivalent weight of sodium thiosulphate is the same as its molecular weight.

The ideas developed in this chapter lead to the following approaches for calculating equivalent weights.

Ion-electron method: The equivalent weight of an oxidant or reductant is the molecular weight divided by the number of electrons which the oxidant or the reductant gains or loses in the reaction. This can be ascertained from the correct partial equations that may be written with the oxidant or reductant:

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$$
$$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O$$
$$2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e$$
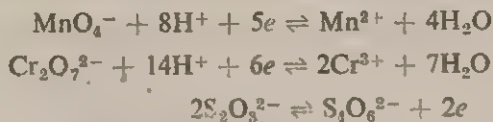
The above ion-electron partial equations give the equivalent weights of permanganate and dichromate as one-fifth, and one-sixth of the respective molecular weights. The equivalent weight of sodium thiosulphate is its molecular weight.

Oxidation number method: The equivalent weight of an oxidant or reductant is given by the molecular weight of the substance divided by the change in oxidation number that the oxidant or reductant suffers in the reaction.

$$\overset{+7}{MnO_4^-} \longrightarrow \overset{+2}{Mn^{2+}}; \qquad \overset{+6}{Cr_2O_7^{2-}} \longrightarrow \overset{+3}{Cr^{3+}}$$
$$\overset{+2}{S_2O_3^{2-}} \longrightarrow \overset{+2.5}{S_4O_6^{2-}}$$
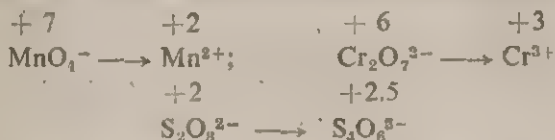
For the thiosulphate the change in oxidation number comes out to be one unit for each mole of sodium thiosulphate (two sulphur in $S_2O_3^{2-}$ has a total of oxidation number of 4 and two sulphur in $S_4O_6^{2-}$ has 5). Thus we arrive at the same result we had from the ion-electron method.

It is to be remembered that *the equivalent weight of a particular oxidant is not a constant quantity. It may change depending on the nature of the oxidation-reduction reaction.* For example, potassium permanganate in acid medium, forces a five electron oxidation but in alkaline medium a three electron oxidation (oxidation of formate to carbonate). Hence in acid medium the equivalent weight is one fifth of the molecular weight and in alkaline medium only one-third of the molecular weight:

$$2KMnO_4 + 3HCOOK = KHCO_3 + K_2CO_3 + 2MnO_2 + H_2O$$
$$MnO_4^- + 2H_2O + 3e \rightleftharpoons MnO_2 + 4OH^-$$
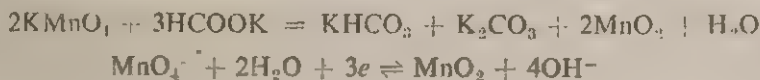
7.10. STANDARD ELECTRODE POTENTIALS AND METAL EXTRACTION PROCEDURES

Standard electrode potentials, as we have already seen, are measures of the reducing ability of the metals or conversely the ease or difficulty of reducing the metal ions to elementary states. The couple with greatest negative potential evidently has a metal ion which is the most difficultly reducible to elementary state. On the other hand the couple with the highest positive potential has a metal ion which is the most easily reducible. For the most difficultly reducible ion we need the most powerful reducing method, and for the most easily reducible ion the

least powerful one will do. From these considerations metal ions can be divided into four categories:

(a) couples with potential more negative than -1.5 volts
(b) couples with negative potential in the range -1.5 to -0.75 volts
(c) couples with negative potentials in the range -0.75 to 0.0 volt
(d) couples with potentials more positive than 0.0 volts.

For metal ions of category (a) electrolysis is used. For elements of category (b) an element with a pronounced affinity for oxygen is used to reduce the metal oxide, for example reduction of Fe^{3+}, Cr^{3+}, ion by Al in thermite process. Carbon reduction is employed for couples of category (c) and simple heating is enough for elements of category (d).

STUDY QUESTIONS

1. The E° values of the couples indicate that MnO_2 cannot oxidise chloride ion to chlorine. Yet it is an experimental procedure in the laboratory to prepare chlorine from chloride ion by oxidation with MnO_2. How do you reconcile? (see chapter 20)

$$Cl_2 + 2e \rightleftharpoons 2Cl^-; \qquad E^\circ = 1.36 \text{ volts}$$
$$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{2+} + 2H_2O; \quad E^\circ = 1.23 \text{ volts}$$
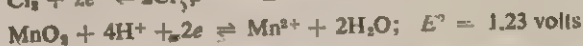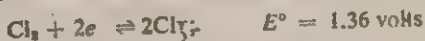
2. For reaction: $I_2 + H_2SO_3 + H_2O \rightarrow HI + H_2SO_4$ (a) state the half reactions (b) state the oxidation numbers of each of the atoms (c) name the oxidant and the reductant and (d) balance the equation by ion-electron method.

3. Perxenate ion XeO_6^{4-} smoothly oxidises manganese (II) to permanganate in acid medium, itself being reduced to XeO_3. Balance the reaction by ion-electron method (see chapter 21).

4. We intend to force the following reaction;

$$A^{2+} + 2e \rightarrow A; \qquad E^\circ = 2.1 \text{ volts}$$

Indicate which of the following couples can force the reaction. (a) B^2/B; $E^\circ = 3.4$; (b) C^{2+}/C, $E^\circ = 1.8$ (c) D^{3+}/D, $E^\circ = -2.8$ (d) E^{3+}/E; $E^\circ = -1.2$ volts.

5. On the basis of E° values choose the two half cells that will produce the (a) highest voltage and (b) the lowest voltage;

Zn^{2+}/Zn (-0.76) ; Mg^{2+}/Mg (-2.37); Cu^{2+}/Cu ($+0.337$); Fe^{2+}/Fe (-0.440); Cd^{2+}/Cd (-0.403) volts.

6. Study the following E° values and predict which would react with acid?

A^+/A; $E^\circ = -1.1$; B^+/B; $E^\circ = 1.2$ and $C^+/C = -2.3$ volts
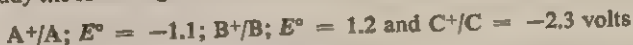
7. Powdered silver metal is added to a solution of $1 M$ $Fe(SCN)_3$. Predict the reaction that might take place. Note that AgSCN is very sparingly soluble. Use these values; E° for Fe^{3+}/Fe^{2+} is $+0.77$ and E° for Ag^+/Ag is $+0.799$ volts.

8. In an aqueous solution containing Fe^{3+} and Fe^{2+} ions, the potential is $+0.70$ volts. Taking the E° value of Fe^{3+}/Fe^{2+} as $+0.77$ volts calculate the Fe^{3+}/Fe^{2+} ratio in the solution.

9. There is no inconsistency or contradiction between the International and American conventions regarding electrode potentials. Comment.

10. Calculate the solubility product of AgCl from the following standard e.m.f.:

$H_2 \mid HCl \mid AgCl, Ag$; $E^\circ = +0.222$ volts. Ag^+/Ag; $E^\circ = +0.799$ volts
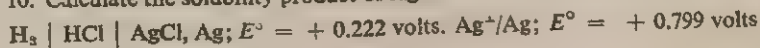
Assume activity of AgCl $= 1$.

$AgCl (s) \rightleftharpoons Ag^+ + Cl^-$ (in solution)

$$K = \frac{[Ag^+][Cl^-]}{[AgCl]} = \frac{[Ag^+][Cl^-]}{1} = K_{SP}$$

The corresponding cell is:

$$Ag, Ag^+ \mid Cl^-; \quad AgCl, Ag \ldots \ldots (E^\circ_{H_2} ; _{H^+} = 0.000)$$

$$E^\circ = E^\circ_{Ag, AgCl, Cl^-} - E^\circ_{Ag, Ag^+}$$

$$= 0.222 - 0.799 = -0.577 \text{ volts}$$

$$\log K_{SP} = \frac{E^\circ}{0.0591} = \frac{-0.577}{0.0591} = -9.8$$

$$\therefore K_{SP} = 10^{-9.8} = 1.6 \times 10^{-10}$$

11. Standard electrode potentials must have a connection with the electronic configurations of the elements. Comment.

12. Study the standard potentials to predict which of the elements potassium and silver is a noble metal. Connect this 'commoner' or 'noble' behaviour with electronic configurations of the elements.

13. A student is asked to name the relative advantages and disadvantages of $KMnO_4$ and $K_2Cr_2O_7$. He writes that $KMnO_4$ is a superior oxidant, is self indicating but cannot serve as a primary standard whereas $K_2Cr_2O_7$ is comparatively weak, needs another indicator but is an excellent primary standard. Comment, elucidate and add new points to make the answer complete.

14. The Hg^{2+}/Hg_2^{2+} couple ($E^\circ = 0.92$ volts) is more oxidising than the Fe^{3+}/Fe^{2+} couple ($E^\circ = 0.77$ volts). Yet Hg_2^{2+} reduces Fe^{3+} to Fe^{2+} in the presence of thiocyanate ion. Comment.

15. $1N \ KMnO_4$ solution may mean 0.33 M or 0.20 M $KMnO_4$. Comment.

16 Given below are the electrochemical cells and their standard reduction potentials. Explain from these data (a) which way electron flows in the outer circuit (b) which electrode functions as the anode and which one as the cathode (c) what will be the e.m.f. of the cell and (d) which of the three metals is the most reducing?

(i) $Zn/Zn^{2+} \parallel Ag^+/Ag$ (ii) $Cd/Cd^{2+} \parallel Zn^{2+}/Zn$

$$Zn^{2+} + 2e \rightleftharpoons Zn; \qquad E^\circ = -0.763 \text{ volts}$$

$$Cd^{2+} + 2e \rightleftharpoons Cd; \qquad E^\circ = -0.431 \text{ volts}$$

$$Ag^+ + e \rightleftharpoons Ag; \qquad E^\circ = +0.799 \text{ volts}$$
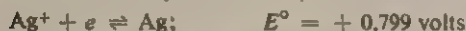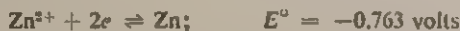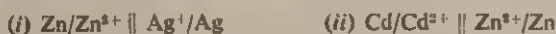
17. Explain the difference between standard potential and formal potential. Present a concise account of the effect of (a) pH and (b) precipitation and (c) complexation on redox potential.

18. Clearly distinguish, with examples, an electrochemical cell and an electrolytic cell. Discuss in this context the two ways lead storage battery behaves.

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Acids and Bases

Our recognition of some chemical substances as acids and certain others as bases rests on some experimental facts about these substances. Acids and bases possess, in a sense, some opposite properties. Acids and bases have been recognised by their effects on some organic dyestuffs. For example, acids turn blue litmus red, and the bases turn red litmus blue. Acids counter the effect of bases and vice versa, the process being called neutralisation. Some acids liberate hydrogen when reacting with some metal ions.

With the passage of time more and more experimental informations accumulated and there arose a need to define acids and bases on a rational basis. The concepts of acids and bases developed one after another tend to make the definitions more and more broad based. In this chapter the different concepts are first described, and then acid-base properties and reactions are considered in water, the most universal solvent available to chemists. We need to be familiar with the following five concepts:

    1. The Arrhenius concept   2. The solvent system concept
    3. The protonic concept   4. The electronic theory
         5. The soft and hard acids and bases principle.

8.1. THE ARRHENIUS CONCEPT

Since Arrhenius was one of the early exponents of the electrolytic dissociation theory, he utilised the dissociation model to define acids and bases. *His classification of acids and bases was based on the theory that acids, when dissolved in water, dissociate into hydrogen ions and anions whereas bases, when dissolved in water, dissociate into hydroxyl ions and cations.*

Acid-base equilibria could now be treated in a quantitative way and acid-base neutralisation could be viewed to result from the union of the hydrogen ions with hydroxyl ions to form water molecules:

$$H^+ + OH^- \rightarrow H_2O$$
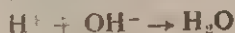
The Arrhenius concept lacks in generality. The most serious limitation is that it recognises dissociation and acid-base reactions in aqueous medium only. It does not recognise the role that non-aqueous solvents can play in the dissociation of acids and bases into ions. According to this concept we cannot regard hydrochloric acid as an acid or an amine as a base in benzene as a solvent. A neutralisation process, therefore, is restricted to aqueous medium alone but many non-aqueous solvents like liquid ammonia, liquid sulphur dioxide etc. are known to initiate comparable acid-base neutralisation processes. The concept also leaves the dissociated hydrogen ion at large, and does not elaborate on its fate in solution. The concept restricts bases merely to hydroxides. Thus even metal oxides would not be regarded as bases.

8.2. THE SOLVENT SYSTEM CONCEPT

Franklin extended the dissociation principles to non-aqueous solvents and realised that non-aqueous solvent molecules may also dissociate into two oppositely charged ions. Thus the two parallel dissociation reactions of water and liquid ammonia can be written as:

$$H_2O \rightleftharpoons H^+ + OH^- \text{ and } NH_3 \rightleftharpoons H^- + NH_2^-$$

Since we now know that a bare proton will readily polarise other anions or molecules, we write a H^+ as H_3O^+ indicating that it is a solvated proton that exists in solution. Similarly H^+ arising out of dissociation of NH_3 will also be solvated:

$$H^+ + H_2O \rightarrow H_3O^+ \text{ and } H^+ + NH_3 \rightarrow NH_4^+$$

so that the overall dissociation of the two solvents will be:

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \text{ and } 2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

Franklin argued that if an acid released H^+ in water to form H_3O^+ ion then an ammonium salt, NH_4Cl, by releasing NH_4^+ in liquid ammonia must also be termed an acid. If NaOH, by virtue of its releasing hydroxyl ion in aqueous medium, is termed a base in that medium, then sodium amide should also be termed a base in liquid ammonia since it releases the amide, NH_2^-, ion. The dissociation (or autoionisation) of non-aqueous solvents is directly responsible for the nature of the chemical reactions that can be initiated in such solvents.

According to the solvent system concept, an acid is a substance which by dissolution in the solvent forms the same cation as does the solvent itself due to autoionisation. A base is one that gives on dissolution in the solvent the same anion as does the solvent itself on its own ionisation. Some neutralisation reactions according to this concept are depicted in Table 8.1. Acid behaviour is not confined to solution containing hydrogen ion alone. Even in non-protonic solvents (e.g. SO_2, $COCl_2$) acid-base neutralisation reactions can be performed. Despite the broader outlook of this concept, it has limitations too. Acid-base phenomena still seem to be dependent on solvents, and that the acid-base reactions still are dictated by the kind of ionisation that the solvent and the reactants undergo.

Table 8.1. Neutralisation Reactions according to The Solvent System Concept

Solvent	Acid	+	Base	→	Salt	,	+	Solvent
H_2O	$H_3O^+(HBr)$		$OH^-(KOH)$		K^+, Br^-			$2H_2O$
NH_3	$NH_4^+(NH_4Br)$		$NH_2^-(KNH_2)$		K^+, Br^-			$2NH_3$
C_2H_5OH	$C_2H_5OH_2^+(HBr)$		$OC_2H_5^-(KOC_2H_5)$		$2K^+$, Br^-			$2C_2H_5OH$
SO_2	$SO^{2+}(SOBr_2)$		$SO_3^{2-}(K_2SO_3)$		$2K^+$, Br^-			$2SO_2$
$COCl_2$	$COCl^+(2COClAlCl_4)$		$Cl^-(CaCl_2)Ca^{2+}$		$(AlCl_4)_2^-$			$2COCl_2$
N_2O_4	$NO^+(NOCl)$		$NO_3^-(AgNO_3)$		Ag^+Cl^-			N_2O_4

8.3. THE PROTONIC CONCEPT

A great advancement was made in the area of acids and bases when Bronsted (and simultaneously Lowry) proposed a new concept which is independent of solvents. *A substance which can split off a proton* (H^+) *was called an acid while a base was a substance which can take up a proton.* A neutralisation process therefore involves a release of a proton by the acid, and the acceptance of that proton by a base. This concept makes acid-base reactions independent of

$$HCl \; + \; NH_3 \longrightarrow Cl^- \; + \; NH_4^+$$
$$\text{acid} \qquad \text{base}$$

$$NH_4^+ \; + \; OH^- \longrightarrow NH_3 \; + \; H_2O$$
$$\text{acid} \qquad \text{base}$$
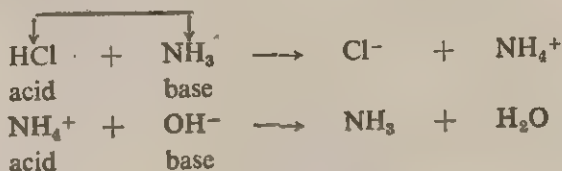
solvent. Neutral compounds or even ions could be designated as acids or bases according to the protonic concept:

$$NH_4^+ \; + \; CH_3COO^- \longrightarrow CH_3COOH \; + \; NH_3$$
$$\text{acid} \qquad \text{base}$$

$$HSO_4^- \; + \; OH^- \longrightarrow HOH \; + \; SO_4^{2-}$$
$$\text{acid} \qquad \text{base}$$

$$HCl \; + \; C_5H_5N \longrightarrow C_5H_5NH^+ \; + \; Cl^-$$
$$\text{acid} \qquad \text{base}$$
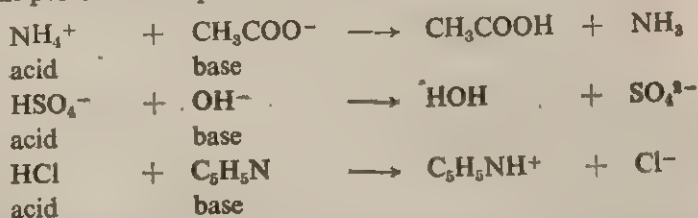
When an acid releases a proton, the residue must be a base, for it is this base that can take up the proton to form the original acid. Therefore any acid-base reaction really involves two acids and two bases, thus forming conjugate pairs. Thus NH_4^+ and NH_3 form a conjugate pair. A conjugate base of an acid is that part left after the proton is lost. Similarly the conjugate acid of a base is the species formed on the addition of a proton to the base. An acid exhibits its acid properties only when it is allowed to react with a base. Similarly a base displays its basic properties only when it is exposed to an acid. Thus effectively all acid-base reactions are results of competitions for protons by bases leading to equilibrium of the type:

$$NH_4^+ \; + \; OH^- \rightleftharpoons HOH \; + \; NH_3$$
$$\text{acid}_1 \qquad \text{base}_2 \qquad \text{acid}_2 \qquad \text{base}_1$$

11

It follows that *the stronger an acid is the weaker is its conjugate base, and the stronger a base is the weaker is its conjugate acid*. Furthermore proton transfer reaction leads to the formation of the weaker acid and the weaker base.

This concept covers a large number and variety of substances under bases, for example, hydroxide ion, amide ion, ethoxide ion, pyridine, alcohols, bisulphate ion, acetate ion and many others. It shows that acid-base phenomena are not dependent on the solvent. Unfortunately, however, by restricting the use of the word acid to proton donors, it fails to recognise several other substances, for example, SO_2, $AlCl_3$, $COCl_2$, $SOCl_2$, etc. which are also known to exhibit acid-base phenomena.

8.4. THE ELECTRONIC THEORY

Each of the three preceding concepts had its own limitations. The need was therefore felt for a concept which can cover all the earlier aspects of acids and bases. Lewis, one of the early exponents of covalent bonding, ultimately succeeded in explaining all hitherto known acid-base reactions by a concept that required the formation of a coordinate link in all such reactions. *A base was to be considered according to Lewis as an electron pair donor and an acid as an electron pair acceptor.* An acid therefore combines with a base leading to a coordinate link from the base to the acid. *An acid must have a vacant orbital into which an electron pair donated by a base can be accommodated. A base, then, is a substance which has at least one unshared (lone) pair of electrons.*

Bronsted concept defined a base as any molecule or ion which accepts proton. Lewis concept recognises that the base has an electron pair to donate to H^+ so that during neutralisation a coordiate bond is formed between the donor atom of the base and the proton. A typical example is:

$$H^+ + \overset{\displaystyle H}{\underset{\displaystyle \ddot{H}}{:\!\ddot{N}\!:\!H}} \rightleftharpoons \left[\overset{\displaystyle H}{H \leftarrow \underset{\displaystyle \ddot{H}}{\ddot{N}\!:\!H}} \right]^+$$
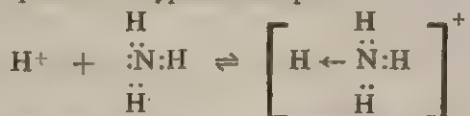
Thus all Bronsted bases are bases in Lewis sense also. All the acids covered by the other concepts are also covered by Lewis definition. Arrhenius considered those substances as acids that could release hydrogen ions (protons). Since the proton can receive an electron pair from a base, all Arrhenius acids are also acids under Lewis definition. The solvent system concept recognises that ammonium chloride should behave as an acid in liquid ammonia. It may be noted that ammonium ion is but an ammoniated proton and the proton can accept a lone pair of electrons from a base. Therefore an ammonium ion in liquid ammonia is also an acid in Lewis sense. The solvent system considers amide ion a base in liquid ammonia. The amide ion is capable of donating a lone pair to an acid, and hence this is a base in Lewis sense. The reaction of NH_4^+ ion and NH_2^- ion in liquid ammonia is represented in Lewis sense as follows:

$$\overset{\displaystyle H}{\underset{\displaystyle \ddot{H}}{H\!:\!\ddot{N}}} + H^+ + \overset{}{\underset{\displaystyle \ddot{H}}{:\!\ddot{N}\!:\!H^-}} \rightarrow \overset{\displaystyle H}{\underset{\displaystyle \ddot{H}}{H\!:\!\ddot{N}}} + \overset{\displaystyle H}{\underset{\displaystyle \underset{\cdot\cdot}{H}}{:\!\ddot{N}\!:\!H}}$$
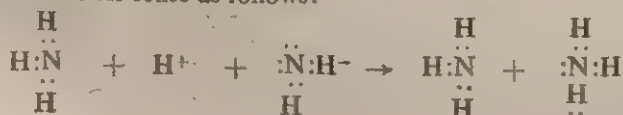
This reaction shows that amide ion is a stronger donor for the proton than ammonia is. Apart from its merit of unifying all previous concepts into one, the concept is very broad indeed in its scope. A wide variety of compounds are recognised as acids and bases according to Lewis. Some examples are cited to elaborate this point.

$$
1. \quad
\begin{matrix}
\text{F} \\
| \\
\text{F--B} \\
| \\
\text{F}
\end{matrix}
\;+\;
\begin{matrix}
\text{H} \\
| \\
:\text{N--H} \\
-| \\
\text{N}
\end{matrix}
\;\rightleftharpoons\;
\begin{matrix}
\text{F} \\
| \\
\text{F--B} \leftarrow
\end{matrix}
\begin{matrix}
\text{H} \\
| \\
\text{N--H} \\
| \\
\text{H}
\end{matrix}
$$
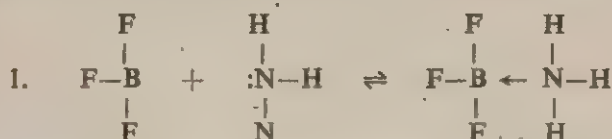
NH_3 behaves as a base and BF_3 as an acid. *Compounds with less than an octet for the central atom (B in BF_3) are Lewis acids.*

$$
2. \quad
\begin{matrix}
:\ddot{\text{O}}: \\
:\ddot{\text{O}}:\ddot{\text{S}} \\
:\ddot{\text{O}}:
\end{matrix}
\;+\;
\begin{matrix}
:\ddot{\text{O}}:\text{H} \\
\ddot{\text{H}}
\end{matrix}
\;\rightleftharpoons\;
\begin{matrix}
:\ddot{\text{O}} \\
:\ddot{\text{O}}\;:\ddot{\text{S}}\;:\ddot{\text{O}}:\text{H} \\
:\ddot{\text{O}}\;:\ddot{\text{H}}
\end{matrix}
$$
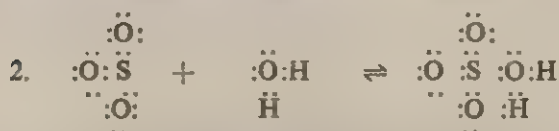
SO_3 is an acid and H_2O a base, SO_3 *like BF_3 has less than an octet, and will be termed an acid according to Lewis.*

3. H^+ (from a proton donor) $+\; :\text{N}\langle\bigcirc\rangle \rightarrow \left[\text{H} : \text{N}\langle\bigcirc\rangle \right]^+$. Pyridine
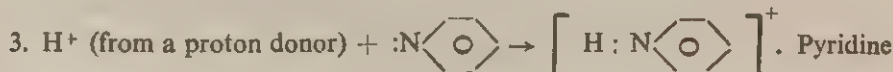
donates an electron pair and thus is a Lewis base. According to solvent system concept pyridine cannot itself ionise and hence the above reaction is not regarded as an acid-base reaction under the solvent system. The reaction of $AsCl_3$ with pyridine can be represented according to Lewis concept as:

$$
\begin{matrix}
\text{Cl} \\
| \\
\text{Cl--As:} \\
| \\
\text{Cl}
\end{matrix}
\;+\; :\text{N}\langle\bigcirc\rangle \;\rightleftharpoons\;
\left[
\begin{matrix}
\text{Cl} \\
| \\
\text{Cl--As:N}\langle\bigcirc\rangle \\
/ \\
\text{Cl}
\end{matrix}
\right]
\;\rightleftharpoons\;
\left[
\begin{matrix}
\text{Cl} \\
| \\
:\text{As:N}\langle\bigcirc\rangle \\
| \\
\text{Cl}
\end{matrix}
\right]^+ + \text{Cl}^-
$$
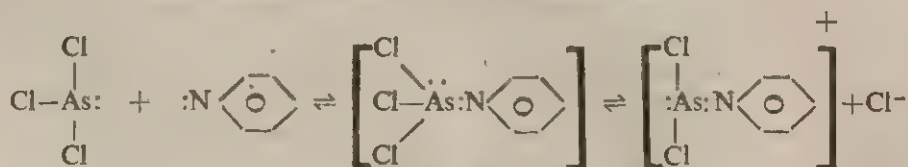
Note that arsenic has an octet in $AsCl_3$. The reaction with pyridine leads first to an intermediate with ten electrons around arsenic. In the final product arsenic returns to octet via release of a chloride ion.

$$
4. \; Cu^{2+} \;+\; 4 \quad
\begin{matrix}
\text{H} \\
| \\
:\text{N--H} \\
| \\
\text{H}
\end{matrix}
\;\rightleftharpoons\;
\left[\text{Cu}\,(:NH_3)_4 \right]^{2+}
$$

$$
5. \; Ag^+ \;+\; 2 \quad
\begin{matrix}
\text{H} \\
| \\
:\text{N--H} \\
| \\
\text{H}
\end{matrix}
\;\rightleftharpoons\;
\left[\text{Ag}\,(:NH_3)_2 \right]^+
$$
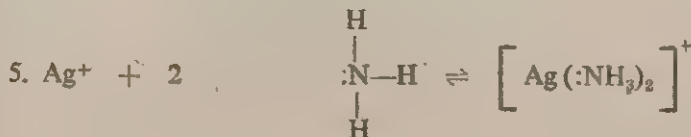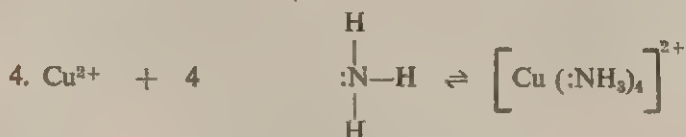
The above reactions leading to the formation of complexes are also acid-base reactions according to Lewis concept. *Metal ions are electron acceptors, that is, acids and the ligands (NH_3 in the above examples) are electron donors, that is, bases. Cations are Lewis acids and anions are bases. Hence salts are acid-base complexes. A Lewis acid is often described as an electrophilic reagent (electron loving) and a Lewis base as a nucleophilic reagent. An electrophilic reagent loves to accept electrons (lone pair) while a nucleophilic (nucleus loving) reagent loves to donate electrons to a nucleus—in fact—to a positively charged ion.*

Unfortunately there is no simple measure of the relative strengths of the bases as electron donors or of the acids as electron acceptors. This is a drawback of Lewis concept compared to the Arrhenius concept or the Lowry concept. In keeping with the latter concepts the relative strengths of acids can be measured in terms of the proton releasing ability. In fact, in aqueous medium dissociation constants of acids (K_A) are invaluable guides to their relative acid character.

8.5. THE SOFT AND HARD ACIDS AND BASES (SHAB) PRINCIPLE

According to Lewis concept an acid-base reaction involves an interaction of a vacant orbital of an acid (A) and a filled, unshared orbital on a base B:

$$A + :B \rightarrow A:B$$

The species A is usually called a Lewis acid or a generalised acid. A strong acid A and a strong base B, will form a stable complex A : B. The Lewis concept has been considerably elaborated to the SHAB principle so that reactions of metal ion towards different ligands can be covered and appreciated.

In order to arrive at a comparative estimate of the donor properties of different bases, the preference of a particular base to bind a proton H^+ and methyl mercury (II) ion, $CH_3—Hg^+$ was determined. Both the proton and the methyl mercury cation can accommodate only one coordinate bond but the two cations vary widely in their preference to bases. This preference was estimated from the experimental determination of equilibrium constants for the exchange reactions:

$$BH^+ + CH_3Hg(H_2O)^+ \rightleftharpoons [CH_3HgB]^+ + H_3O^+$$
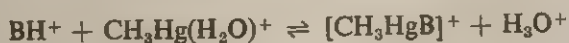
The results indicate that bases in which the donor atom is N, O, or F prefer to coordinate to the proton. Bases in which the donor atom is P, S, I, Br, Cl or C prefer to coordinate to mercury. *The donor atoms in the first group have high electronegativity, low polarisability and are hard to oxidise. Such donors have been named 'hard' bases by Pearson, since they hold on to their electrons strongly. The donor atoms of the second category are of low electronegativity, of high polarisability, and are easy to oxidise. Such donors have been called 'soft' bases since they hold on to their valence electrons rather loosely.* Table 8.2 provides a classification of various bases into hard, soft or borderline bases. It will be noted that chloride ion is less soft than bromide, which again is harder than the iodide ion.

Table 8.2. Classification of Bases (R = alkyl or aryl group)

Hard	Soft
H_2O, OH^-, F^-, CH_3COO^-, PO_4^{3-}, SO_4^{2-}, Cl^-, CO_3^{2-}, ClO_4^-, NO_3^-, ROH, RO^-, R_2O, NH_3, RNH_2, N_2H_4	R_2S, RSH, RS^-, I^-, SCN^-, $S_2O_3^{2-}$, R_3P, R_3As, $(RO)_3P$, CN^-, RNC, CO, C_2H_4, C_6H_6, H^-

Borderline

$C_6H_5NH_2$, C_5H_5N, N_3^-, Br^-, NO_2^-, SO_3^{2-}, N_2

After having gone through a classification of the bases, a classification of Lewis acids is necessary. The preference of a given Lewis acid (say a metal ion) towards ligands of different donor atoms is usually determined from the stability constant values of the respective complexes (say, $[Cu(NH_3)_2]^+$ and $[Cu(PR_3)_2]^+$) or from some other useful equilibrium constant measurements. When this is done, metal complexes with different donor atoms can be classified into two sets based on the sequences of their stabilities:

I. Class (a) acids or hard acids: $N \gg P$; $O \gg S$; $F > Cl > Br > I$

II. Class (b) acids or soft acids: $N \ll P$; $O \ll S < Se$; $F < Cl < Br < I$

Lewis acids can now be classified into three categories: hard, soft and borderline acids (Table 8.3).

Table 8.3. Classification of Lewis Acids

Hard	Soft
H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+}, Al^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, La^{3+}, Lu^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}, Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}, U^{4+}, Ce^{3+}, Sn^{4+}, VO^{2+}, UO_2^{2+}, MoO^{3+}, BF_3, $AlCl_3$, SO_3, Cr^{6+}	Cu^+, Ag^+, Au^+, Tl^+, Hg^+, Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, CH_3Hg^+, Tl^{3+}, BH_3, $GaCl_3$, $InCl_3$, I^+, Br^+, I_2, Br_2, Zerovalent metal atoms

Borderline

Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Sn^{2+}, Sb^{3+}, Bi^{3+}, Rh^{3+}, $B(CH_3)_3$, SO_2, NO^+, GaH_3

Hard acids have small acceptor atoms, are of high positive charge and do not contain unshared pairs of electrons in their valence shell, although all these properties may not appear in one and the same acid. These properties lead to high electronegativity and low polarisability. In keeping with the naming of the bases, such acids are termed 'hard' acids. On the contrary, soft acids have large acceptor atoms, are of low positive charge and contain unshared pairs of electrons in their valence shell. These properties lead to high polarisability and low electronegativity. Again in keeping with the naming of the bases, such acids are termed 'soft'.

Soft acids form stable complexes with bases that are highly polarisable, are good reducing agents and not necessarily good bases towards the proton. Hard acids, on the other hand, usually form stable complexes with bases that binds well with protons.

If the donor atoms of the most common bases are arranged in the order of increasing electronegativity the following order is obtained:

As,	P	< C,	Se,	S,	I	< Br	< N, Cl	< O	< F
2.0	2.1	< 2.5	2.4	2.5,	2.5	< 2.8	< 3.0, 3.0	< 3.5	< 4.0
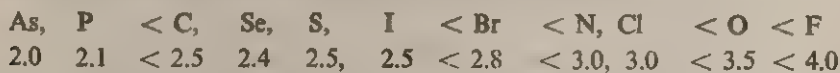
Soft Lewis acids will form more stable complexes with left hand members of this series and hard Lewis acids will form more stable complexes with the right hand members. Ahrland and Chatt have termed the hard acid metal ions as class 'a' metals/acceptors and the soft acid metal ions as class 'b' metals or acceptors.

Experimental data on various complexes of soft and hard acids and bases indicate a simple rule: *Hard acids prefer to bind hard bases and soft acids prefer to bind soft bases.*

The SHAB concept is extremely useful in elucidating many properties of the chemical elements and will be often referred to at appropriate places. Some interpretations will now be made in the light of this concept. In both BF_3 and BH_3 the boron is trivalent but quite different behaviour is noted. The presence of hard fluoride ions in BF_3 makes it easy to add other hard bases e.g.: $H_3N \rightarrow BF_3$. The presence of soft hydride ions in BH_3 makes it easy to add other soft bases. In BF_3 the boron is nearly B^{3+}. But the soft hydride ions donate negative charges extensively to boron, so that the boron atom is almost neutral and becomes soft. For elements of variable valence there is usually an increase in hardness with Increase in oxidation state. Thus nickel (0) in $Ni(CO)_4$ is soft, nickel (II) is borderine and nickel (IV) is hard. Nickel (II) forms both nitrogen and sulphur complexes whereas nickel (IV) is stabilised mostly by oxygen donor ligands like periodate :$K[Ni(IO_6)]$. Although nickel (III) and nickel (IV) are also known to be stabilised by o-phenylenebisdimethylarsine (diars), the complexes also contain hard Cl^- ions in the coordination zone, $[NiCl_2(diars)_2]^{2+}$. The sulphur end of the thiocyanate ion is assumed to be softer than the nitrogen end, and hence prefers soft Lewis acids. A study was made of the complexing ability of both an alkyl thiocyanate, RSCN, and an alkyl isothiocyanate, RNCS, with the soft Lewis acid iodine, and the hard Lewis acid phenol. The thiocyanate, RSCN, with a free nitrogen end to act as a donor, formed more stable complex with phenol than with iodine. With the isothiocyanate exactly opposite results were obtained.

8.6. THE FATE OF THE PROTON IN AQUEOUS MEDIUM

The proton plays a key role in acid-base functions. In aqueous medium it is usually represented as H_3O^+. A naked hydrogen ion has a vanishingly small size (radius $\sim 10^{-13}$ cm $= 10^{-5}$ A) and therefore has a very high charge/radius ratio ($\sim 10^5$) and is expected to be the most effective in polarising other ions or molecules according to Fajans' rules. In H_3O^+ there is assumed a coordinate

bond from water oxygen to the proton, thus giving the proton a helium electronic configuration.

Experimental evidences are available in support of such formulations. Thus perchloric acid, $HClO_4$, reacts vigorously with water. It gives a series of hydrates: $HClO_4$, (M.P. °C)−112°; $HClO_4$. H_2O. + 50°; $HClO_4$. $2H_2O$, −17.8°; $HClO_4$. $3H_2O$, −37°; $HClO_4$. $3.5H_2O$, −41.4°. Of these hydrates the most remarkable is the monohydrate, melting at a much higher temperature than the covalent, anhydrous acid. It is very stable, and can be heated to around 110° without decomposition. The monohydrate is about ten times as viscous as the anhydrous acid. It has the same crystal lattice as the ionic ammonium perchlorate, showing that it, too, is an ionic compound, $[H_3O]$ $[ClO_4]$.

Besides the H_3O^+ species, a species $H_9O_4^+$, $[H^+(H_2O)_4]$ with a tetrahedral arrangement of four water dipoles around a proton is also known. However H_3O^+ is the dominating form and the proton in aqueous medium is represented in this form.

8.7. WATER AS AN ACID AND AS A BASE: CONCEPT OF K_w

We have already learnt that water dissociates weakly to H^+ and OH^- ions. Regardless of what other ions are present in water, there will always be an equilibrium between H^+ and OH^- ions:

$$H_2O \rightleftharpoons H^+ + OH^-$$

The proton, however, will be solvated and is usually written as H_3O^+. For simplicity we will write H^+ only. The above equilibrium will have its own equilibrium constant:

$$K = \frac{[H^+] [OH^-]}{[H_2O]} \text{ or } K \times [H_2O] = [H^+] [OH^-]$$

The square brackets indicate concentrations. Recognising the fact that in any dilute aqueous solution, the concentration of the water molecules ($= 55.5$ moles/litre) greatly exceeds that of any other ion, $[H_2O]$ can be taken as a constant. Hence,

$$K \times [H_2O] = K_w = [H^+] [OH^-]$$

where K_w is the dissociation constant of water (ionic product of water). The value of $[H^+]$ in pure water has been determined as $10^{-7}M$ so that K_w becomes 1.0×10^{-14}. The above relation tells us that in aqueous solution the concentrations of H^+ and OH^- are inversely proportional to each other. If H^+ concentration increases 100 fold, that of OH^- has to decrease 100 fold to maintain K_w constant. Dissociation of H_2O into H^+ and OH^- ions is an endothermic reaction:

$$H_2O + 13.7 \text{ KCal} \rightarrow H^+ + OH^-$$

Thus, according to Le Chatelier's principle, increasing temperature will facilitate dissociation, thus giving higher values of K_w. The values of K_w at 20°C, 25°C and 60°C are 0.68×10^{-14}, 1.00×10^{-14} and 9.55×10^{-14} respectively.

8.8. THE CONCEPT OF pH

The dissociation constant of water, Kw, has such a low value that expressing the concentrations of H^+ and OH^- ions of a solution in terms of such low figures is not much convenient and meaningful. Such expressions necessarily have to involve negative powers of the base 10. Sorensen proposed the use of a term known as pH, defined as:

$$pH = -\log_{10}[H^+] = \log_{10}\frac{1}{[H^+]}$$

Thus a solution having a H^+ concentration of 10^{-1} M has a pH 1 and that of 10^{-14} M has a pH 14. For such solutions having H^+ concentrations in the range 10^{-1} M to 10^{-14} M it is more convenient and meaningful to express acidity in terms of pH rather than H^+ concentrations. The use of small fractions or negative exponents can thus be avoided. It is obvious that for a monobasic acid molarity and normality are the same while they are different for a polybasic acid. Thus $0.1M$ H_2SO_4 is really $0.2N$ H_2SO_4 so that $pH = -\log_{10}[H^+] = -\log_{10}(0.2) = 0.699$. The corresponding expression for the hydroxide ion is:

$$pOH = -\log[OH^-]$$

It follows from these relations that the lower the pH, the more acidic the solution is. If the acidity of a solution goes down 100 fold its pH goes up by two units. For example, a solution of pH 1 has $[H^+]$ which is 100 times greater than that of pH 3. Taking the case of OH^- ions, the pOH will go down by two units (from 13 to 11). Recalling that the product of $[H^+]$ and $[OH^-]$ is 10^{-14} and that this has to remain constant we can write the following steps:

$$[H^+] [OH^-] = 10^{-14}$$
$$\log [H^+] + \log [OH^-] = \log 10^{-14} = -14$$
$$pH + pOH = 14$$

We can now proceed to differentiate between neutral, acidic or basic solutions on the basis of relative concentrations of H^+ and OH^- ions on the one hand, and on the basis of pH on the other. A neutral solution is one in which the concentrations of H^+ and OH^- ions are equal:

$$[H^+] = [OH^-] = (10^{-14})^{\frac{1}{2}} = 10^{-7}M$$

An acidic solution is one in which concentration of H^+ exceeds that of OH^-:

$$[H^+] > [OH^-]; [H^+] > 10^{-7}M; [OH^-] < 10^{-7}M$$

A basic solution is one in which concentration of OH^- exceeds that of H^+:

$$[OH^-] > [H^+]; [OH^-] > 10^{-7}M; [H^+] < 10^{-7}M$$

In terms of pH we have the following relations:

neutral solution   : $[H^+] = 10^{-7}M$; $pH = 7.0$
acidic solution   : $[H^+] > 10^{-7}M$; $pH < 7.0$
basic solution   : $[H^+] < 10^{-7}M$; $pH > 7.0$

Table 8.4 summarises [H$^+$], [OH$^-$], pH and pOH relationship and shows how they affect the neutrality of water.

Mathematical definition of pH provides a negative value when [H$^+$] exceeds 1 M. However pH measurements of such concentrated solutions are avoided. as these solutions are not likely to be dissociated fully. Concentration of such strongly acid solutions is best expressed in terms of molarity than in terms of pH.

Table 8.4. The Scale of pH

[H$^+$]	pH	[OH$^-$]	pOH	
10^0	0	10^{-14}	14	
10^{-1}	1	10^{-13}	13	
10^{-2}	2	10^{-12}	12	
10^{-3}	3	10^{-11}	11	acid solution
10^{-4}	4	10^{-10}	10	
10^{-5}	5	10^{-9}	9	
10^{-6}	6	10^{-8}	8	
10^{-7}	7	10^{-7}	7	neutral solution
10^{-8}	8	10^{-6}	6	
10^{-9}	9	10^{-5}	5	
10^{-10}	10	10^{-4}	4	
10^{-11}	11	10^{-3}	3	basic solution
10^{-12}	12	10^{-2}	2	
10^{-13}	13	10^{-1}	1	
10^{-14}	14	10^0	0	

8.9. STRENGHTHS OF ACIDS AND BASES

Relative strengths of Brönsted acids can be appreciated by comparing their tendency to donate protons to a given base. The obvious choice of a base for purposes of comparison is water. Hydrochloric acid in this solvent reacts essentially completely to give the solvated proton:

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

But HF does so only incompletely:

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$

The reaction of hydrocyanic acid is even more incomplete, so that most of the HCN remains in the undissociated, molecular form. We thus observe that HCl is a stronger acid than HF, which again is stronger than HCN in aqueous medium.

Solvent plays a significant role in determining the relative strength of acids. All strong acids like HCl, HBr, HClO$_4$ react completely with water to produce H$_3$O$^+$. In aqueous solution the strongest acid, in the Brönsted sense, that can exist is H$_3$O$^+$. All acids stronger than H$_3$O$^+$ react with water completely to produce this acid. The medium water, thus, has a levelling effect on all strong acids. Such a solvent therefore cannot distinguish between strong acids. In another rd, water is too strong a base to allow us to test the relative strengths of very

strong acids. It is obvious that solvents which are still more basic than water, for example ammonia, will be even poorer choice for such purposes of comparison. Conversely, acidic solvents, such as anhydrous sulphuric acid, acetic acid will allow the determination of the acid strengths of very strong acids. These solvents are far weaker bases than water (in fact these are acids) so that complete dissociation of the so called strong acids will not occur. In anhydrous acetic acid, for example, the following order of decreasing acid strength has been determined:

$$HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$$

This discussion shows that there is no absolute basis of designating the strengths of acids. Although the strengths of very strong acids cannot be determined in water, strengths of weak acids have been successfully determined in this solvent. For weak acids water is not quite strong a base to completely convert the weak acid to H_3O^+. In other words water behaves as a base of strength comparable to that of the conjugate base of the weak acid.

Similar levelling effect is also noticed on the basic strength. The strongest acids that can exist in the solvents— water, anhydrous sulphuric acid and anhydrous ammonia—are respectively H_3O^+, $H_3SO_4^+$ and NH_4^+. The strongest bases in these solvents are respectively OH^-, HSO_4^- and NH_2^-. The bases O^{2-} and NH_2^- are stronger bases than OH^-. Therefore just as all very strong acids are all converted into H_3O^+ in water, so also all very strong bases O^{2-} and NH_2^- ions will react with water completely to form OH^- ions. The following reactions of Na_2O and $NaNH_2$ in water are essentially complete in aqueous medium. Therefore

$$O^{2-} + H_2O \rightarrow 2OH^-$$
$$NH_2^- + H_2O \rightarrow NH_3 + OH^-$$

the basic strength of oxides or amides cannot be determined in aqueous solution. This time water is quite strong an acid to force complete reaction. Therefore the basic strength of such bases must be determined in solvents of lower acid character like liquid ammonia. Other bases such as NH_3, $HCOO^-$ do not react completely with water to form OH^- but exist in aqueous solution in equilibrium so that the basic strengths of these bases may be determined in aqueous medium.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
$$HCOO^- + H_2O \rightleftharpoons HCOOH + OH^-$$

Since the dissociation of an acid involves an equilibrium between the undissociated form and the dissociated form, the experimental determination of the equilibrium constant will give us a quantitative measure of the relative strength of the acid. For the case of a weak acid HA we have:

$$HA \rightleftharpoons H^+ + A^- ; \quad K_A = \frac{[H^+][A^-]}{[HA]}$$
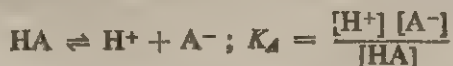
where $[H^+]$, $[A^-]$ and $[HA]$ are the measured equilibrium concentrations of the H^+ (in water H_3O^+), A^- and the undissociated HA. K_A is called the acid dissociation constant of the acid. The stronger the acid, the larger will be its K_A. In

equimolar solutions of two different acids, the concentrations of H^+ ion will be greater for the acid of larger dissociation constant. Just as we used the term pH to express the concentration of H^+ ion, so also pK_A is used to express the dissociation of an acid.

$$pK_A = -\log_{10} K_A = \log_{10} \frac{1}{K_A}$$

Therefore *the larger the value of pK_A, the weaker the acid is.* Conversely *the smaller the value of pK_A the stronger the acid is.*

Dissociation of weak bases in aqueous medium may also be treated in a manner completely analogous to that used with weak acids. The dissociation of ammonia may be expressed as:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \; ; \; K_B = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$
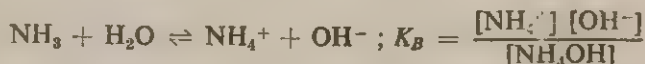
K_B represents the basic dissociation constant of the weak base. The basic dissociation of the acetate ion in water will take the form:

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^- \; ; \; K_B = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$
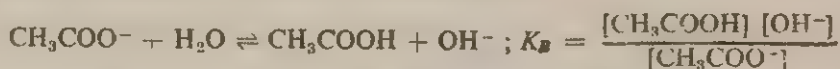
The acid dissociation constant of a weak acid HA, and the basic dissociation constant of the anion A^- are connected as follows:

$$K_A \times K_B = Kw = 1.0 \times 10^{-14}$$

The relation can be readily checked by taking the example of acetic acid. We have the following relations:

$$K_A = \frac{[H^+]+[CH_3COO^-]}{[CH_3COOH]} \text{ and } K_B = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$K_A \times K_B = [H^+][OH^-] = Kw = 1 \times 10^{-14}$$

Table 8.5 lists the dissociation constants of some common acids and bases in aqueous medium.

The reader may check that the data in Table 8.5 obey the relation $K_A \times K_B = Kw = 1.0 \times 10^{-14}$. In the Table the dissociation constants of the acids $HClO_4$, HCl, H_2SO_4, HBr, HNO_3 have been marked as large. For such acids the dissociation in water is virtually complete so that the concentration of undissociated acid approaches zero. It is therefore not possible to calculate a numerical value for K_A since zero in the denominator will lead to infinity. For weak acids the situation is entirely different and the solution contains measurable quantities of H^+, A^- and HA.

Experimental determination of K_A or K_B is based on the determination of the concentration of H^+ or OH^- in an aqueous solution of a known concentration of the acid or base. A platinum electrode is dipped into the solution and hydrogen gas bubbled through. Thus a half cell is generated. This half cell is connected through a salt bridge to a standard hydrogen electrode. The potential difference in volts is recorded by connecting the two electrodes via a voltmeter. This poten-

Table 8.5. Dissociation Constants of common Acids and Bases

Acid	K_A	Acid Strength	Base	K_B	Base Strength
$HClO_4$	large	strong	CH_3COO^-	5.6×10^{-10}	weak
HCl	large	strong	NH_3	1.8×10^{-5}	weak
HBr	large	strong	CN^-	2.5×10^{-5}	weak
HI	large	strong	F^-	1.4×10^{-11}	weak
HNO_3	large	strong	HS^-	1.0×10^{-7}	weak
H_2SO_4	large	strong	S^{2-}	1.0×10^1	weak
H_2SO_3	1.7×10^{-2}	weak	NO_2^-	2.2×10^{-11}	weak
HSO_4^-	1.3×10^{-2}	weak	$H_2PO_4^-$	1.3×10^{-12}	weak
H_3PO_4	7.5×10^{-3}	weak	HPO_4^{2-}	1.6×10^{-7}	weak
HF	7.0×10^{-4}	weak	HSO_3^-	5.9×10^{-13}	weak
HNO_2	4.5×10^{-4}	weak			
CH_3COOH	1.8×10^{-5}	weak			
H_2S	1.0×10^{-7}	weak			
$H_2PO_4^-$	6.3×10^{-8}	weak			
HCN	4.0×10^{-10}	weak			
NH_4^+	5.7×10^{-10}	weak			
H_2O	1.0×10^{-14}	weak			
HS^-	1.0×10^{-15}	weak			

tial difference is used to calculate the concentration of H^+ in the experimental solution. For this a standard curve (Fig. 8.1) is made use of, wherein the potential difference between a standard hydrogen electrode ($E^\circ = 0.00$ volt) and a hydrogen electrode in solutions of different, known concentrations of H^+ is plotted. Thus the concentration of H^+ is found out. Once [H^+] is known, concentrations of A^- ([A^-]) and that of undissociated HA ([HA]) can be calculated with a knowledge of the starting concentraion of the acid. With the discovery of glass electrode and calomel electrodes direct determinations of pH of a solution have turned out to be routine affairs. Specially prepared soft glasses are permeable to hydrogen ions only, and this property is the basis of glass electrodes. There are other standard methods also for such determinations. A popular technique is to determine the concentration from optical density measurements of HA in acid and alkaline solutions. Such techniques are useful where HA and A^- differ widely in their absorption characteristics so that optical density measurements can be confidently analysed to determine the concentrations of HA and A^-.

Relevant to the above exposition of the acid dissociation constant of an acid HA is the well known Henderson equation. A weak acid HA dissociates in aqueous solution as:

$$HA \rightleftharpoons H^+ + A^-$$
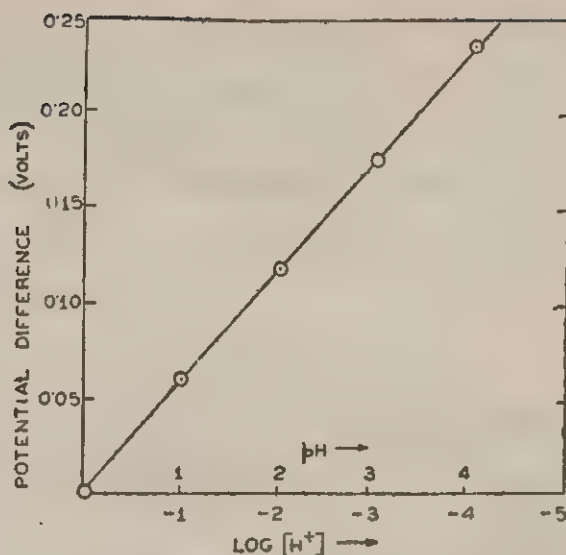
FIG. 8.1. Potential difference between a standard hydrogen electrode and a hydrogen electrode in solutions of different concentrations of H^+ plotted against pH

so that $[H^+] = \dfrac{[HA]}{[A^-]} \times K'_A$ where K_A is the equilibrium constant. The equilibrium in solution will apply equally to the dissociation of the pure acid alone as well as to a solution of HA in presence of added H^+ ions or added A^- (in the form of a salt MA). Then in a solution containing HA and MA of concentration C_A and C_S we have: concentration of undissociated acid = [HA] = initial concentration of the acid—concentration of $H^+ = C_A - [H^+]$.

  Concentration of A^- in solution '
  = concentration of A^- arising out of the dissociation of MA
    + concentration of A^- due to dissociation of the acid HA
  = $C_S + [H^+]$

Then $[H^+] = \dfrac{C_A - [H^+]}{C_S + [H^+]} \times K_A$ [MA is completely dissociated]; HA being a weak acid, $[H^+]$ is small compared to C_A and C_S so that

$$[H^+] = \frac{C_A}{C_S} \times K_A = K_A \times \frac{[Acid]}{[Salt]}$$

Then $$pH = -\log [H^+] = -\log K_A - \log \frac{[Acid]}{[Salt]}$$

$$= pK_A + \log \frac{[Salt]}{[Acid]}$$

This means if we titrate a weak acid to half way to its neutralisation point then log [Salt]/[Acid] becomes zero and therefore the pH of the half neutralisation point provides the pK_A of the acid. The above equation is called the Henderson equation.

8.10. ACIDITY FUNCTION

In acid dissociation constant, K_A of a weak acid in aqueous medium we have a quantitative measure of the acid strength of the acid. Such K_A values cannot be obtained for strong acids in aqueous solutions due to their complete dissociation. In acidity function Hammett has found a quantitative measure of the acidity of strong acids.

Hammett's approach utilises the dissociation of an uncharged (neutral) base B (for example, p-aminoazobenzene) in strong acids. The equilibrium between B and BH^+ is expressed as:

$$K_A = \frac{[B][H^+]}{[BH^+]} \cdot \frac{f_B f_{H^+}}{f_{BH^+}}$$

where K_A is the thermodynamic dissociation constant of the acid BH^+ and f_B, f_{H^+}, f_{BH^+} represent the respective activity coefficients. The activity coefficients cannot be predicted in concentrated solutions of BH^+ in the solvent. However, since BH^+ and B differ only by a H^+, the ratio f_B/f_{BH^+} will be the same irrespective of B. Then a quantity h_0 is given by:

$$h_0 = K_A \cdot \frac{[BH^+]}{[B]} = [H^+] \frac{f_{H^+} f_B}{f_{BH^+}}$$

Now h_0 turns out to be a property of the solution irrespective of the nature of B and of its concentration. If B is a suitable organic compound that changes colour on being protonated, the ratio $[BH^+]/[B]$ can be easily determined colorimetrically, and K_A obtained from measurements in dilute solution. Hammett has found H_0 (called acidity function), the negative logarithm of h_0, to be more useful for comparison of acid strength of different acids in different solvents:

$$H_0 = -\log_{10} h_0 = pK_A + \log_{10} \frac{[B]}{[BH^+]}$$

In dilute solutions the f's are unity so that $h_0 = [H^+]$ and hence $H_0 = $ pH. But in concentrated solution H_0 of different acids of same molarity show considerable difference in the values of H_0 to make H_0 a suitable yardstick for comparison of strong acids. Some typical H° values are: $+7.0$ for water, -1.5 for $6M$ aqueous HNO_3, -2.0 for $6.9\ M$ aqueous HCl, -2.63 for $8\ M$ aqueous $HClO_4$, -5.54 for 70% aqueous H_2SO_4 and -10.60 for 100% H_2SO_4. Thus 100% H_2SO_4 is over $100,000$ times as efficient a proton donor as 70% aqueous H_2SO_4 (change in $H_0 = 10.60 - 5.54 = 5.06$). Thus acidity function affords a comparison of the strength of very strong acids.

8.11. ACID-BASE INDICATORS

In aqueous medium acidity is due to the presence of H^+. The H^+ concentration of an acidic aqueous solution can be reduced by the addition of OH^- ions whence the two react to form neutral H_2O. This process of removal of H^+ ion by OH^- ions or vice versa is called neutralisation, and is an important part of

common laboratory operations. Such neutralisation processes are followed by a sharp change of colour of some organic compounds, called acid-base indicators, at the point of neutralisation.

Acid-base indicators are usually weak organic acids with complex structures. Such organic acids possess different colours in their undissociated, and in dissociated forms and fortunately the change from the undissociated to the dissociated forms (or vice versa) occurs over a short pH range. Taking HIn as the formula of the indicator the dissociation can be written as:

$$HIn \rightleftharpoons H^+ + In^-; \quad K_A = \frac{[H^+] \ [In^-]}{[HIn]}$$

This dissociation process will be facilitated if the liberated H^+ ions are removed by reaction with say OH^-. On the other hand this dissociation will be suppressed on the addition of H^+ ions. Therefore the undissociated form HIn of the indicator is favoured in acid medium, and the dissociated form In^- in alkaline medium.

When a few drops of the indicator HIn are added to water an equilibrium is established. The solution attains a certain colour, which is a blending of the colours of HIn and In^-. If the K_A value of the indicator is large, then the colour of In^- predominates. If K_A is small, the colour of HIn predominates. Therefore a suitable acid-base indicator in a neutralisation titration will indicate by a change of colour the point where the solution changes suddenly from an acidic to a basic side (or vice versa).

Taking an example of the indicator, bromothymol blue (HIn; $K_A = 1 \times 10^{-7}$) which has a yellow colour in the HIn form and a blue colour in the anion In^- form we have:

$$K_A = \frac{[H^+] \ [In^-]}{[HIn]} = 1 \times 10^{-7}$$

when the $[In^-] = [HIn]$, $[H^+]$ is equal to $K_A = 1 \times 10^{-7}$

This means at pH 7, bromothymol blue will have a colour intermediate between yellow and blue, that is, a green colour. In acid solution ($[H^+] > 10^{-7}$) bromothymol blue will exist primarily in the yellow form of HIn molecule and in alkaline solution ($[H^+] < 10^{-7}$) the blue colour of the In^- predominates. For the determination of K_A or pK_A of an indicator, a series of solutions of the same volume and the same amount of the indicator are prepared. The pH of these solutions are adjusted to different values from acid to the alkaline range. In practice it is more convenient to take buffer solutions of a range of known pH values. The same amount of the indicator is added to the buffer solutions. The pH of that very solution whose colour is just intermediate between the acid colour and the alkaline colour of the indicator corresponds to the pK_A of the indicator. However this is a very rough method.

The pH ranges of acid-base indicators have been determined carefully. Table 8.6 gives some commonly used acid-base indicators. The pH, $[H^+]$ or $[OH^-]$ of a given aqueous solution may be determined by a judicious use of one or more of the indicators mentioned in Table 8.6.

Table 8.6. Some Acid-Base Indicators

Indicator	pH interval for Colour Change	Acid Colour	Base Colour
Methyl yellow	2.9 — 4.0	Red	Yellow
Methyl orange	3.1 — 4.4	Red	Yellow
Bromocresol green	3.8 — 5.4	Yellow	Blue
Methyl red	4.4 — 6.2	Red	Yellow
Litmus	4.5 — 8.3	Red	Blue
Thymolphthalein	8.3 — 10.5	Colourless	Blue
Phenolphthalein	8.5 — 10.0	Colourless	Pink
Thymol blue	8.0 — 9.6	Yellow	Blue
Bromothymol blue	6.0 — 7.6	Yellow	Blue
Bromophenol blue	3.0 — 4.6	Yellow	Blue
Alizarin yellow R	10.1 — 12.0	Yellow	Violet

For example, if one finds that a solution does not develop a pink colour with phenolphthalein, its pH must be below 8.5. But if the solution is yellow with methyl red then the pH of the solution must be above 6.2.

Suitable mixing of certain indicators leads to a universal indicator which develops different colours at different pH. Universal indicators are not useful for quantitative titrations but may be used for a rough idea of the pH of a solution. One such indicator may be prepared by dissolving 0.1 g of phenolphthalein, 0.2 g of methyl red, 0.3 g of methyl yellow, 0.4 g of bromothymol blue and 0.5 g thymol blue in 500 ml ethanol and adding sodium hydroxide solution to make the solution just yellow. The colour changes of this mixed indicator are: red at pH 2; orange at pH 4; yellow at pH 6; green at pH 8 and blue at pH 10. Strips of paper impregnated with a mixture of several suitably chosen indicators have been designed so as to give gradations of colour over a wide or a narrow pH range. Such papers are called pH papers and are in frequent use in chemical laboratories.

Table 8.7. Recommended Indicators for Acid-Base Titrations

Nature of Titration	pH change at around the equivalence point	Recommended Indicator
Strong Acid with Strong Base	4 — 10	Methyl orange, methyl red, phenolphthalein, bromothymol blue, thymolphthalein, etc.
Weak Acid with Strong Base	8.7 — 10.5	Phenolphthalein, thymolphthalein, thymol blue.
Weak Base with Strong Acid	3 — 6.5	Methyl red, methyl orange, bromophenol blue, bromocresol green.
Weak acid with weak Base	7.0	No suitable indicator.

8.12. VARIATION IN ACIDIC AND BASIC PROPERTIES

So far we have devoted mainly to the different concepts of acids and bases, and to the quantitative expression of acidity and basicity in aqueous medium. Another feature of acids and bases that interests us is how acidity and basicity should vary with respect to the position of the elements in the Periodic Table. The answer to this query is not given simply. We will, however, endeavour to state certain rules along with some explanations. The discussion for the sake of clarity is given under three heads:

8.12.1. Hydracids: The dissociation of binary hydracid HX, to take a simple example, in solution consists of the following steps:

1. HX (solution) → HX (gas)   2. HX (gas) → H (gas) + X (gas)
3. H (gas) → H⁺ (gas) + e (gas)   4. X (gas) + e → X⁻ (gas)
5. H⁺ (gas) → H⁺ (solvated)   6. X⁻ (gas) → X⁻ (solution)

All acids have steps (3) and (4) in common and the energy involved in step (1) is small for most acids. Therefore variation in acidity of simple hydracids depends mostly on:

(1) the energy of dissociation of the hydride to give the two atoms.
(2) electron affinity of the atom X
(3) the solvation energy of the anion

Although all the three factors are involved, in the first short period increasing electron affinity of the elements with increasing atomic number predominates over the other two factors. As a consequence the acidity of the hydracids increases along the period. The first step acid dissociation constant ($K_A{}^I$) of some hydrides are shown below:

Hydracid	CH_4	NH_3	H_2O	HF
$K_A{}^I$	10^{-58}	10^{-35}	10^{-14}	10^{-4}

In the series of halogen hydracids electron affinity tends to decrease from fluorine to iodine. This should really have led to a decrease in the acidity of their hydracids. Experimental studies, instead, have revealed the following order of acidity:

$$HI > HBr > HCl > HF$$

The apparent anomalous behaviour is explained on the consideration of the single bond energy of the hydracids, which decreases from HF to HI. The dissociation

Hydracid	HF	HCl	HBr	HI
Single bond energy (Kcal/mole)	135	103	88	71

energy takes an upper hand over the other two factors. This result also emerges when we consider that besides the decrease in electron affinity from F to I, there is a distance factor involved. The hydrogen in HI is far removed from the nucleus of the iodine atom than it is from the nucleus of the fluorine atom (H—I bond length = 1.70 A; H—F bond length = 1.01 A). This increased separation encourages dissociation or enhanced acidity along the series HF to HI.

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The behaviour of the hydracids of group VI B is also similar as would appear from the following data:

Hydracid	H_2O	H_2S	H_2Se	H_2Te
K_A^I	1×10^{-14}	1×10^{-7}	1.7×10^{-4}	2.3×10^{-3}
Single bond energy (Kcal/ mole)	111	81	66	59

Whereas the hydracids of group VI B and VII B give protons in aqueous solution, those of group V B are far less acidic. In fact NH_3 accepts proton from water and thus behaves as a base ($NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$; $K_B = 1.8 \times 10^{-5}$). The other hydrides are much less basic and have very little tendency to accept protons from water molecules. PH_3 forms a phosphonium iodide only when reacted with a strong acid such as HI. Single bond energies of NH_3 and PH_3 are 93 and 76 Kcal/mole and thus the bond energy takes the primary role.

8.12.2 Oxyacids: A strongly electronegative element bonded to hydrogen will tend to pull away electron density from around hydrogen, thus facilitating dissociation. The greater the electronegativity of the central atom of the oxyacid the more it will pull electrons from oxygen on to itself. The oxygen in its turn will pull electrons from hydrogen. Thus dissociation of an oxyacid is dictated more by the electronegativity of the central atom than by the other factors. This line of argument is validated by the following trends of acidity of some oxyacids:

$$HClO_4 > HIO_4 \; ; H_2SO_3 > H_2SeO_3 \; ; HOCl > HOBr > HOI$$

An increase in the formal charge (oxidation number) of the central atom of the oxyacid leads to an increase in the acidity, as in the following series of chlorine oxyacids:

$$HClO_4 > HClO_3 > HClO_2 > HClO$$

This increase in formal charge is brought about by the addition of electronegative oxygen atoms to the central atom. Note that all these four acids have one protonated oxygen, that is, one —OH. The unprotonated oxygen atoms by virtue of their strong electronegative character tend to withdraw electron density from around hydrogen through the intervening central atom (inductive effect). The following series of acids also follow this pattern:

$$H_2SO_4 > H_2SO_3 \; ; HNO_3 > HNO_2$$

In this context the phosphorus oxyacids are interesting. The formal charge rule predicts an order which is the reverse of what has been obtained experimentally (predicted: $H_3PO_4 > H_3PO_3 > H_3PO_2$; experimental, $H_3PO_2 > H_3PO_3 > H_3PO_4$). The dilemma is solved when we take a good look at their structures:
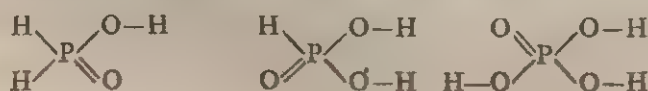
H_3PO_2 is a monobasic acid. The proton attached to an oxygen has a far greater chance of dissociation than any directly bonded hydrogen. The structure of H_3PO_2 involves one protonated oxygen and another unprotonated oxygen. H_3PO_3 is dibasic and hence has two protonated oxygens and one unprotonated oxygen. H_3PO_4 is tribasic, has three protonated oxygens and one unprotonated oxygen. In this series therefore the number of unprotonated oxygens, which are the vehicles for enhancement of acidity, is the same (namely one) for all the three acids. But the number of protonated oxygen atoms and consequently the number of dissociable protons increase from one in H_3PO_2 to three in H_3PO_4. Therefore the overall inductive effect of the unprotonated oxygen decreases from H_3PO_2 to H_3PO_4. Hence the acidity slightly falls off in the order shown. The following Table 8.8 lists some acid dissociation constants of oxyacids.

Table 8.8. Acid Dissociation Constants of Some Oxyacids

Acid	K_A or K_A^{I}	Acid	K_A or K_A^{I}
HClO	3.2×10^{-8}	HIO	5×10^{-13}
$HClO_2$	1×10^{-2}	HBrO	2×10^{-9}
$HClO_3$	Large	HClO	3.2×10^{-8}
$HClO_4$	Very large	H_2TeO_3	6×10^{-6}
H_2SO_3	1.7×10^{-2}	H_2SeO_3	3×10^{-3}
H_2SO_4	Very large	H_2SO_3	1.7×10^{-2}
HNO_2	4.5×10^{-6}	H_3PO_4	7.5×10^{-3}
HNO_3	Very large	H_3PO_3	1.6×10^{-2}
		H_3PO_2	6×10^{-2}

It should be noted that for polybasic acids the successive dissociation constants gradually fall off. This is because splitting off a proton from a neutral uncharged acid is easier than it is from a negatively charged ion. The following data prove the point:

Acid	K_A^{I}	K_A^{II}	K_A^{III}
H_2S	1×10^{-7}	1×10^{-15}	
H_2SO_3	1.7×10^{-2}	5.6×10^{-8}	
H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	1.7×10^{-10}

8.12.3. Periodic Variations in Acidity and Basicity: In the series of binary hydrides CH_4, NH_3, H_2O and HF it has been observed that the electron affinity of the central element takes precedence over other factors, thus explaining the acid character. The increase in acid character of the hydroxides along a period from left to right is admirably shown by the following series:

Period	I	II	III	IV	V	VI	VII
	NaOH	Mg(OH)	Al(OH)	Si(OH),	H.PO,	H.SO,	HClO,

It is well known that the left hand members are strongly basic, the right hand ones are strongly acidic and the central region ones are amphoteric in nature. According to Arrhenius concept NaOH is a strong base because in aqueous solution hydroxide ions are generated. That NaOH does not dissociate into NaO^- and H^+ ions is due to the attraction between O^{2-} and the very small H^+ being much stronger than the attraction between O^{2-} and the much larger Na^+. As the charge on the central element increases the attraction between O^{2-} and the central element becomes significant enough to make the dissociation into OH^- ions difficult. In other words, increasing charge on the central element enhances its electronegativity so that it can form strong covalent bond with oxygen. When this happens chances are that dissociation will generate proton and not hydroxide ion.

A movement along a group in the Periodic Table with the elements in a given oxidation state can only increase the size of the ions. This effect reduces the electronegative character, and provided electronegativity takes control over other factors, we would expect a decrease in acidic character. Effectively in a group the basic character of the oxides (also of the elements) should increase with increasing atomic number. This is a general rule which holds good to some extent in all groups of the Periodic Table. Thus in group VB nitrogen (III) phosphorus (III) oxides are acidic, arsenic (III) and antimony (III) oxides are amphoteric and bismuth (III) oxide is only basic.

Aquo metal ions also will develop acidity depending on the size and charge of the metal ion. In the light of the discussions made so far it is not difficult to appreciate that acidity will be enhanced by small size and large charge on the cation. Under favourable conditions one or more protons may dissociate from the coordinated aqua groups:

$$[M(H_2O)_6]^{n-} + H_2O \rightleftharpoons [M(H_2O)_5(OH)]^{n-1} + H_3O^+$$

For M = Fe(III) the equilibrium constant of the above hydrolysis reaction is $\sim 10^{-3}$, whereas for M = Fe(II) the value is expectedly lower. The equilibrium constants for M = Al(III), Cr(III) and Fe(III) are $\sim 10^{-5}$, $\sim 10^{-4}$ and $\sim 10^{-3}$ respectively, the ionic radii being Al^{3+} (0.5A), Cr^{3+} (0.64A) and Fe^{3+} (0.67A). There appears to be as yet no satisfactory rule regarding the quantitative values of the acidities of hydrated metal ions.

Summing up we have the following working rules with respect to the variation of acidity and basicity in the Periodic Table:

1. Acid properties increase with increasing atomic number along a period. This is due to enhanced electronegativity.

2. Acid properties decrease or conversely basic properties increase with increasing atomic number along a group. This is mainly due to decrease in electronegativity.

3. Acid properties of hydracids of a particular group increase with increasing atomic number. Bond energies of the hydracids decrease down a group and this effect outweighs electronegativity effect.

4. The higher the electronegativity of the central atom of an oxyacid the higher is the acidity.

5. The higher the formal charge (oxidation number) of the central atom of the oxyacid the higher is the acidity.

6. The higher the charge on the cation and the lower the size of the cation. the higher is the acidity of its aqua complex.

8.13. ENHANCEMENT OF ACIDITY DUE TO INDUCTIVE EFFECT AND RESONANCE

Substitution at suitable points in organic compounds has helped us a lot in gaining further insight into variations in acidity. On substituting a halogen atom for a hydrogen atom in acetic acid, the strength of the acid is enhanced. This enhancement of acid strength appears to bear a relation with electronegativity of the halogen. Since the halogens are more electronegative than carbon, such substitution makes the carbon slightly positive, which in turn tends to drag electron density from the other carbon. The carboxylic carbon again makes the protonated oxygen atom slightly positive, which effect assists the dissociation of the proton. It follows the higher the electronegativity of the halogen the more pronounced will be the effect. If instead of introducing electron withdrawing groups (such as halogens), electron releasing groups (such as CH_3^-) are introduced, acidity will decrease. The two cases can be represented as shown below, where δ^- and δ^+ stand for the (fractional) negative charge and (fractional) positive charge respectively. Starting with a δ^+ (or δ^-) on the first carbon, the charge density will decrease to the next carbon and further so in the protonated oxygen. This trend is indicated by increased δ's and is known as *inductive effect. Inductive effect may be defined as the effect transmitted by a charged atom at one point in an ion or a molecule to another point in the same ion or molecule.* The inductive influence of electron attracting groups is expressed as $-$ I. On the other hand electron releasing groups increase electron density on the carbon atom at which these are attached. Such inductive effects are expressed as $+$ I.

$+$ I : $-CH_3$; $-CH_2R$; $-CR_3$; (R alkyl group)

$-$ I : $-F$; $-Cl$; $-Br$; $-I$; $-NO_2$; $-C_6H_5$;.
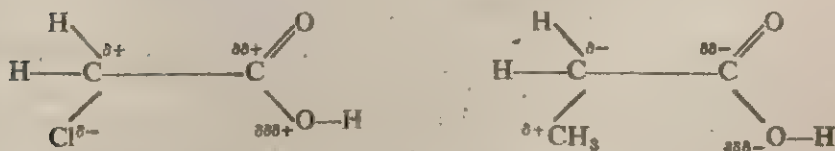
The dissociation constants of some organic acids (Table 8.9) are given to show these inductive effect.

Table 8.9. Acid Dissociation Constants of Some Organic Compounds

Acid	K_A	Acid	K_A
CH_3COOH	1.8×10^{-5}	Cl_3CCOOH	2.24×10^{-1}
FCH_2COOH	2.2×10^{-3}	CH_3-CH_2COOH	1.32×10^{-5}
$ClCH_2COOH$	1.38×10^{-3}	$(CH_3)_3CCOOH$	8.92×10^{-6}
$Cl_2CHCOOH$	5.01×10^{-2}	C_6H_5OH	1.12×10^{-10}

Besides these inductive influences, there is another very important source that also contributes substantially to the acidity. A molecule or an ion for which several resonance structures can be written gains extra stability (Chapter 5). It is well known that carboxylic acids, for example acetic acid, are far stronger acids than alcohols. It will be noted that for the carboxylate anion it is possible to write the following two resonance structures:

Such equivalent resonance structures cannot be written for the acid itself since resonance forms must not change the position of the different atoms. Thus the carboxylate anion is stabilised, which facilitates the dissociation of the proton. Similarly phenol also admits of two resonance structures for its ions and accordingly this behaves as an acid.
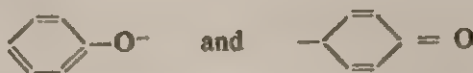
Similar reasoning would show that aniline is a weaker base than alkylamines.

8.14. Hydrolysis: This may be defined as the interaction between the ions of water and a salt of a weak acid or a salt of a weak base. Such interaction leads to the production of (i) a weak acid or a weak base or (ii) of both a weak acid and a weak base. In general terms hydrolysis may be expressed as:

$$MA + H_2O = MOH + HA$$
$$Salt + Water = Base + Acid$$
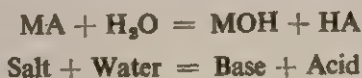
The nature of the product solution will be dictated by the properties of MOH and HA. If the strength of MOH as a base is weaker than the strength of HA as an acid the product solution will be acidic in nature. Thus the hydrolysis of a salt (MA) of a weak base (MOH) and a strong acid HA will lead to acid reaction. Conversely hydrolysis of a salt (MA) of a strong base (MOH) and a weak acid (HA) will produce a basic solution. Thus hydrolysis of NH_4Cl and CH_3COONa will produce respectively an acid reaction and alkaline reaction.

8.15. Buffers: Buffer solutions may be defined as those solutions whose pH remains virtually unchanged upon the addition of small amounts of strong acids or bases. It can be guessed immediately that such solutions should have as their constituent substances which can consume H^+ or OH^- ions producing only very weakly dissociated acids or bases such that the original pH of the buffer solutions are not affected to any appreciable extent. Thus buffer solutions consist of solutions of a weak acid HA and its sodium or potassium salt (NaA or KA) or of a weak base B and its salt BH^+. *Thus a buffer solution may also be stated as a solution which is made up of an acid and its conjugate base or a base and its conjugate acid.*

A solution having sodium acetate and acetic acid in certain proportion will make a buffer solution. If a few drops of a solution of a strong base NaOH is added, then these dissociated OH^- ions will be consumed by the weak acid CH_3COOH.

$$OH^- + CH_3COOH \rightarrow H_2O + CH_3COO^-$$

thus resisting any change in the pH of the system. Addition of a few drops of a strong acid, HCl, will force a reaction of the H^+ ions with the acetate ions resulting in the formation of the weakly dissociated acetic acid:

$$H^+ + CH_3COO^- \rightarrow CH_3COOH$$
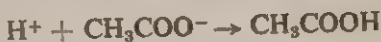
Thus the buffer solution will once again resist any change in its pH value. Buffer solutions can be diluted without appreciable change in the H^+ concentration.

Two points should be appreciated in respect of buffer solutions:

1. The capacity of a buffer to absorb H^+ and OH^- ions without any appreciable change in pH is limited by the concentrations of the weak acid and weak base making up the buffer.

2. A buffer system is capable of maintaining a relatively constant pH in a rather narrow range.

To calculate the pH of a buffer solution made up of a weak acid and its salts we can apply the Henderson equation:

$$pH = pK_A + \log \frac{[Salt]}{[Acid]}$$

If the concentration of the salt and the acid in the above relation is the same we have $pH = pK_A$. Therefore if we wish to make a buffer solution of a particular pH we should look for a weak acid whose pK_A is close to the desired pH. Thus for a buffer of pH around 5 a mixture of acetic acid ($K_A = 1.8 \times 10^{-5}$; $pK_A = 4.74$) and ammonium acetate will be a good choice.

For a mixture of a weak base (of dissociation constant K_B) and its salt with a strong acid we will have the following parallel equation:

$$pOH = pK_B + \log \frac{[Salt]}{[base]}$$

Buffer solutions come to the aid of chemists whenever it becomes obligatory

to study some reactions or reaction rates at a constant pH. For example the oxidation of iodide ion by H_2O_2 is $[H^+]$ dependent:

$$2I^- + H_2O_2 + 2H^+ \rightarrow I_2 + 2H_2O$$

If the pH is maintained constant it becomes possible to study the effect of the concentration of I^-, the temperature etc.

Suitable combinations of the following chemicals will produce buffer solutions:
  (a) acetic acid-ammonium acetate
  (b) disodium hydrogen phosphate—potassium dihydrogen phosphate
  (c) ammonium chloride—ammonium hydroxide.

8.16. SOME PROBLEMS RELATED TO ACIDS AND BASES

Problem: pH of a solution is 4.5. Calculate the concentration of H^+ ion.
$$pH = -\log [H^+] = 4.5; \quad \therefore \log [H^+] = -4.5 = \bar{5}.5$$
The number corresponding to the antilogarithm of 0.5 is 3.16.
$$\therefore [H^+] = \text{antilog of } \bar{5}.5 = 3.16 \times 10^{-5}$$

Problem: Calculate the $[H^+]$, $[OH^-]$ and pH of a solution prepared by diluting 20 ml of $0.1M$ HCl to one litre.

$$[H^+] = \frac{20 \times 0.1}{1000} = 0.002 = 2 \times 10^{-3}$$

$$[OH^-] = \frac{1 \times 10^{-14}}{[H^+]} = \frac{1 \times 10^{-14}}{2 \times 10^{-3}} = 0.5 \times 10^{-11}$$

$$pH = -\log [H^+] = -\log (2 \times 10^{-3}) = -\log 2 + 3 = 2.7$$

Problem: Calculate the $[H^+]$, $[OH^-]$ and pH of a solution obtained by dissolving 32.0 gm KOH to make 200 ml of a solution.

$$[OH^-] = \frac{32.0 \times 1000}{56.0 \times 200} = 2.86 \, M \text{ (molecular weight of KOH 56.0 gm)}$$

$$[H^+] = \frac{1 \times 10^{-14}}{2.86} = 0.35 \times 10^{-14}$$

$$pH = -\log (0.35 \times 10^{-14})$$
$$= -\log 3.5 + 15 = -0.54 + 15 = 14.46$$

Problem: A buffer solution contains 0.10 mole of CH_3COOH and 0.10 mole CH_3COO^- per litre. (1) Calculate the pH of the buffer, (2) Calculate the pH after the addition of 0.01 mole/lit of HCl, (3) Calculate the pH after addition of 0.01 mole/lit of NaOH. [$K_A = 1.8 \times 10^{-5}$].

(1) $\qquad K_A = \dfrac{[H^+] [CH_2COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$

Since $[CH_3COO^-] = 0.1\ M$ and $[CH_3COOH] = 0.1\ M$

we have: $[H^+] = 1.8 \times 10^{-5} = K_A$

$\therefore\ pH = -\log_{10}[H^+] = -\log(1.8 \times 10^{-5})$

$= -(0.26 - 5.00 = 4.74$

(2) Now $[H^+] = 0.01\ M$

$$H^+ + CH_3COO^- \to CH_3COOH$$

$\therefore\ [H^+] = 1.8 \times 10^{-5} \times \dfrac{[CH_3COOH]}{[CH_3COO^-]} = 1.8 \times 10^{-5}\dfrac{(0.1 + 0.01)}{(0.01 - 0.01)}$

$= 1.8 \times 10^{-5} \times \dfrac{(0.11)}{(0.99)} = 2.2 \times 10^{-5}$

$\therefore\ \ pH = 4.66$

Alternatively Henderson equation may also be applied.

[Salt] = original concentration of CH_3COO^- minus the added acid (as the H^+
will combine with CH_3COO^- to form undissociated CH_3COOH).
$= 0.10 - 0.01 = 0.09$

[Acid] = original concentration of CH_3COOH plus the newly formed CH_3COOH
$= 0.10 + 0.01 = 0.11$

$$pH = pK_A + \log \frac{[Salt]}{[Acid]} = -\log(1.8 \times 10^{-5}) + \log \frac{0.09}{0.11}$$

$$= 4.74 - 0.09 = 4.65$$

(3) Now $[OH^-] = 0.01\ M$

$$OH^- + CH_3COOH \to H_2O + CH_3COO^-$$

$[CH_3COOH] = 0.01 - 0.01 = 0.09$

$[CH_3COO^-] = 0.01 + 0.01 = 0.11$

$\therefore\ [H^+] = 1.8 \times 10^{-5} \times \dfrac{[CH_3COOH]}{[CH_3COO^-]}$

$= 1.8 \times 10^{-5} \times \dfrac{(0.09)}{(0.11)} = 1.5 \times 10^{-5}$

$\therefore\ \ pH = 4.82$

Applying Henderson equation we have:

$$pH = pK_A + \log \frac{[Salt]}{[Acid]} = -\log(1.8 \times 10^{-5}) + \log \frac{0.11}{0.09}$$

$$= 4.82$$

Problem: The dissociation constant of NH_4OH is 2.0×10^{-5}. What will be the OH^- concentration of an aqueous solution which is $0.1\ M$ with respect to NH_4OH and $0.1 M$ with respect to NH_4Cl?

(a) $K_B = \dfrac{[NH_4^+][OH^-]}{[NH_4OH]} = 2 \times 10^{-5}$

$\therefore$ $[OH^-] = \dfrac{K_B[NH_4OH]}{[NH_4^+]} = \dfrac{2 \times 10^{-5} \times 0.1}{0.1} = 2 \times 10^{-5}M$

In view of the low K_B value it has been assumed that the NH_4OH does not disso-
ciate to any significant extent.

(b) $pOH = pK_B + \log \dfrac{[Salt]}{[Base]} = pK_B + \log \dfrac{0.1}{0.1} = pK_B$

$\therefore [OH^-] = K_B = 2 \times 10^{-5}M$

Problem: In dilute aqueous solution H_2SO_4 is completely dissociated into
H^+ and HSO_4^- ions. The second step dissociation constant has a value of
1.2×10^{-2}. Calculate the concentrations of H^+, HSO_4^- and OH^- ions in 1.00
litre solution containing 0.100 mole of H_2SO_4.

Note that the total H^+ ions will be coming from both the dissociation steps.
Let x be the concentration of H^+ coming from the second step. Then x will also
be the concentration of SO_4^{2-}.

Total $[H^+] = 0.1 + x$; $[SO_4^{2-}] = x$

$K_A^{II} = \dfrac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = \dfrac{(0.1+x)x}{0.1-x} = \dfrac{0.1x + x^2}{0.1-x} = 1.2 \times 10^{-2}$

Neglecting x^2 we have:

$0.1\,x = 0.1 \times 1.2 \times 10^{-2} - (1.2 \times 10^{-2})x$

$0.112\,x = 1.2 \times 10^{-3}$ $\therefore$ $x = \dfrac{1.2 \times 10^{-3}}{0.112} = 0.01\ M$

$\therefore$ Total $[H^+] = 0.1 + 0.01 = 0.11\ M$

$[SO_4^{2-}] = 0.01\ M$

$[HSO_4^-] = 0.1 - 0.01 = 0.09\ M$

$[OH^-] = \dfrac{1 \times 10^{-14}}{0.11} = 9 \times 10^{-14}\ M$

Problem: K_A for HY is 1.0×10^{-7}. Calculate the OH^- of an $0.01\ M$ solution
of a salt KY. What is the pH of the solution?

$K_A \times K_B = K_W = 1 \times 10^{-14}$; $K_B = \dfrac{1 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-7}$

K_B of $Y^- + H_2O \rightleftharpoons HY + OH^-$ is 1.0×10^{-7}

Thus $K_B = \dfrac{[HY] \times [OH^-]}{[Y^-]} = 1.0 \times 10^{-7}$

$[OH^-] = \dfrac{K_B \times [Y^-]}{[HY]}$

But $[HY] = [OH^-]$ and $[Y^-] = 0.1$ since KY is a fully dissociated salt.

$[OH^-][HY] = [OH^-]^2 = K_B \times [Y^-] = 1 \times 10^{-7} \times 10^{-1} = 1 \times 10^{-8}$

$\therefore [OH^-] = 1 \times 10^{-1} M; \quad \therefore pOH = 4; \quad \therefore pH = 14-4 = 10$

Ostwald's Dilution Law: This law tells us how the dissociation of weak electrolytes (i.e. incompletely dissociated electrolytes) in solution is influenced by dilution. Acetic acid, for example, is a weak electrolyte and dissociates as follows:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

This dissociation has a characteristic equilibrium constant, K_A, specifically called acid dissociation constant. Let us assume that 1 mole of acetic acid is dissolved in v litres of water, so that its concentration is 1/v moles/litre. We further assume that a fraction, a, of this acid has undergone dissociation. Since we started with 1 mole, then a mole (fraction) has dissociated; $(1-a)$ mole has remained undissociated. a is also called the degree of dissociation. We can write the following relation:

$$K_A = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(a/v) \times (a/v)}{(1-a)/v} = \frac{a^2}{(1-a)v} = \frac{a^2c}{(1-a)}$$

where c is the concentration of the original CH_3COOH ($c = 1/v$ moles/litre).

This relation predicts that as we go on diluting a solution of a weak electrolyte, c gradually decreases and hence in order to maintain K_A constant, α has to increase in the numerator. α being small compared to 1 may be neglected in the denominator. Thus we see *with dilution the degree of dissociation of a weak electrolyte increases.* This is Ostwald's dilution law. Strong electrolytes (e.g. NaCl) are wholly dissociated in solution and hence do not come under the purview of Ostwald's dilution law.

STUDY QUESTIONS

1. CF_3COOH is a very strong acid and $(CF_3)_3N$ has no basic properties. Is there any common cause?

2. $HClO_4$ is a very strong acid in aqueous medium. In what solvents would it behave as a moderately strong or weak acid?

3. $HClO_4$, HBr, HNO_3 are strong acids in aqueous medium. NaH, $NaNH_2$ and $NaOC_2H_5$ are also strong bases. Explain.

4. Thiocyanate is an ambidentate ligand (Chapter 10). Do you think weakly basic metals should bond to thiocyanate at the S end and basic metals through nitrogen?

5. The pH of blood is 7.40. Calculate the ratio of bicarbonate to carbonic acid (K_A^I of $H_2CO_3 = 4.5 \times 10^{-7}$).

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-; \quad K_A^I = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$\therefore \frac{[HCO_3^-]}{[H_2CO_3]} = \frac{K_A^I}{[H^+]} = \frac{4.5 \times 10^{-7}}{[H^+]} = \frac{4.5 \times 10^{-7}}{3.98 \times 10^{-8}} \simeq 11$$

(pH = 7.40; $-\log[H^+] = 7.40$; $\log[H^+] = -7.40 = \bar{8}.6$

$[H^+] = $ antilog of $\bar{8}.6 = 3.98 \times 10^{-8}$)

6. Which is the strongest protonic acid in the series? (a) NH_3, PH_3, SbH_3 (b) SnH_1, SbH_3, H_2Te (c) $[Fe(H_2O)_6]^{3+}$, $[Fe(H_2O)_6]^{2+}$, H_2O.

7. Which are the strongest Lewis acids in the series? (a) BF_3, BCl_3, BI_3 (b) $BeCl_2.BCl_3$.

8. In order that a protonic acid can function as an acid conditions must be favourable for the solvation of the proton. Comment.

9. The dissociation constant of an indicator acid is 1×10^{-6}. The undissociated acid has a red colour, the anion form has a yellow colour. What will be the colour of the indicator in a solution of pH 4, 6 and 8?

10. BCl_3 cannot function as a Lewis base. Comment.

11. Tricovalent phosphorus compounds can serve as Lewis bases and also as Lewis acids. Comment (see also Chapter 18).

12. Ammonia is a base according to Lowry-Brönsted concept and also according to Lewis theory. Comment.

13. The reaction HCl (aq) + KOH (aq) → KCl (aq) + H_2O is neutralisation according to (a) Lowry-Brönsted concept (b) Lewis theory and (c) solvent system concept. Comment.

14. An acid is an electron pair acceptor and a base an electron pair donor. Elucidate.

15. For each metal the lower oxidation states are basic and the higher oxidation states are acidic. Comment.

16. You are given 10 ml of 0.1 M HCl. How would you make solutions of (a) pH 1.0 (b) pH 3.0 and (c) pH 7.0?

17. 105 g. of HN_3 is dissolved to produce one litre of a solution of pH 2.0. Calculate the dissociation constant of the acid.   (Ans. = 4.1×10^{-4})

18. Classify the following into acids and bases following the electronic theory: (a) NH_4^+ (b) H^+ (c) D_2O (d) H^- (e) $(CH_3)_2SO$

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Non-aqueous Solvents

Much of our chemical knowledge has been gathered from studies in aqueous medium. Water has some very useful solvent characteristics: wide availability, wide liquid range, ease of handling and its ability to dissolve ionic compounds. These qualities have made water a universal solvent. Chemists, however, have extended their studies to other non-aqueous solvents as well. The concepts of acids and bases developed in the previous chapter are useful in an appreciation of the chemical reactions in non-aqueous solvents.

9.1. CLASSIFICATION OF SOLVENTS

A common classification of solvents is based on the proton-donor and proton-acceptor properties of the solvents. The following Table 9.1 shows three types of solvents—protic, aprotic and amphiprotic.

Table 9.1. Types of Solvents

Solvent type	Proton donor/proton acceptor character	Examples
1. Protic		
(a) acidic (protogenic)	(a) tendency to release proton	HF, H_2SO_4, CH_3–$COOH$, HCN
(b) basic (protophilic)	(b) tendency to accept proton	NH_3, amines, N_2H_4
2. Aprotic	No tendency either to release or to accept protons	C_6H_6, $CHCl_3$, SO_2, CCl_4
3. Amphiprotic	tendency to release or to accept protons depends on the nature of the reacting species	H_2O, ROH

Protic solvents carry hydrogen in their formula and may be predominantly either acidic (HF) or basic (NH_3). Aprotic solvents may or may not carry hydrogen in their formula. They do not release proton nor accept proton. Amphiprotic solvents have hydrogen as one of their constituents, and can exhibit both acidic and basic properties depending on the nature of the reacting species. Such solvents dissociate feebly into protons and anions. Water and alcohols are amphiprotic solvents.

Another alternative way of looking into the classification of solvents is based on the solvent system concept of acids and bases (section 8.2). In this form of classification the solvents can generate through autoionisation a particular set of cation and anion. Solutes which can break up to produce the same cation as the solvent itself does will be termed as acids and those which can give the corresponding anion will be designated as bases. Thus in liquid ammonia ($2NH_3 \rightarrow NH_4^+ + NH_2^-$) ammonium salts are acids while amides are bases. Similarly in liquid SO_2 ($2SO_2 \rightarrow SO^{2+} + SO_3^{2-}$) thionyl halides behave as acids ($SOCl_2 \rightarrow SO^{2+} + 2Cl^-$) while sulphites ($K_2SO_3 \rightarrow 2K^+ + SO_3^{2-}$) as bases. Such classification effectively means sorting out of a set of parent solvents for particular solutes.

Solvents may also be classified from another viewpoint. Some solvents are suitable for dissolving ionic compounds and for initiating ionic reactions. Such solvents are called ionising (or ionic) solvents (H_2O, NH_3, HF etc.). There are other solvents which cannot dissolve ionic compounds nor can initiate ionic reactions. They are suitable for dissolving non-ionic, neutral compounds, and are called non-ionising solvents (C_6H_6, CCl_4 etc). Ionising solvents are themselves polar whereas the non-ionising solvents are non-polar.

Since no ionic reactions can be studied in non-ionising solvents, the solvent properties of such solvents are mostly confined to dissolution of non-ionic compounds. In this chapter we are concerned with the examination of some ionising solvents and to begin with, some qualities of ionising solvents will be enumerated.

9.2. QUALITIES OF IONISING SOLVENTS

An ionic compound is a compact assemblage of positively charged cations and negatively charged anions. The process of dissolution of such a compound in a solvent must involve a separation of the cation and anion. A weakening of the electrostatic attraction between the two ions must be brought about, and this is realised through a judicious choice of a solvent. The force of attraction (F) between two charged spheres (q^+ and q^-) separated by a distance r, in a medium of dielectric constant D, is given by:

$$F = \frac{1}{D} \cdot \frac{q^+ q^-}{r^2}$$

Dielectric constant may be viewed as a proportionality constant. The relation immediately shows that for the same q^+, q^- and r the force will be smaller the larger the dielectric constant of the solvent. Thus a good ionising solvent must have a high dielectric constant. For instance water has a high dielectric constant

(78.5) and therefore is a good solvent for ionic compounds. The positive ions (say Na^+) of an ionic solute (NaCl) are attracted by the negative dipolar end of H_2O $\left(\begin{array}{c} H^+ \\ \\ H^+ \end{array}\!\!\!\!> O^{--}\right)$ and the negative ions (Cl^-) are attracted by the positive end of the aqua molecules. Thus NaCl passes into solution in water. *A solvent of high dielectric constant effectively reduces the attraction of the oppositely charged ions of the ionic solute for each other, thus facilitating dissolution.* It is imperative that in order to have a solute dissolve in an ionic solvent, the solute must itself be ionic. This explains why a non-polar substance does not dissolve in ionic solvents like water.

The reader should note that solvent-solute interaction leading to solubility is more involved than would appear from a series of dielectric constants alone. Other factors that might have specific influence in specific cases are ion-dipole, dipole-dipole, hydrogen-bonding and even π-complexing interactions.

Thus H_2SO_4 (dielectric constant 85) and HF (dielectric constant 84) are quite good solvents for many organic molecules. Evidently the organic molecules act as bases:

$$\begin{array}{c} CH_3 \\ \\ CH_3 \end{array}\!\!\!\!> C = O + H_2SO_4 \rightarrow \begin{array}{c} CH_3 \\ \\ CH_3 \end{array}\!\!\!\!\overset{\delta+}{>}C = \overset{\delta-}{O}H^+ + HSO_4^-$$
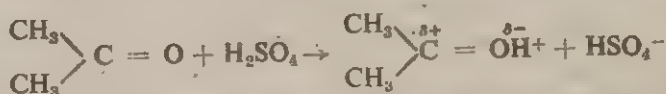
Acetonitrile (dielectric constant 36) readily forms complexes with copper (I) and silver (I) iodide resulting in their dissolution although these salts are insoluble in water. Lithium iodide and also NiI_2, $NiBr_2$ are soluble in solvents such as acetonitrile, dichloroethylene because of formation of complex species $[NiI_4]^{2-}$, $[NiBr_4]^{2-}$. Silver perchlorate is soluble in benzene to provide crystals of $AgClO_4$. C_6H_6. Structure determination has revealed that Ag^+ ion is closely associated with a double bond of the aromatic ring—indicating some π-type interaction between the filled metal d-orbital with empty π^* orbital of the aromatic ring. The high solubility of iodides in liquid ammonia may also be ascribed, at least in part, to hydrogen bonding.

Table 9.2 records the viscosity, dielectric constant, autoionisation and the ionic products of some common ionising solvents. Viscosity of the solvent often influences the usefulness of the solvent. Mobility of ions depends on viscosity, mobility decreasing with increasing viscosity. Solvents of low viscosity can be handled rather easily. Precipitation, crystallisation and filtrations are carried out, on the other hand, with considerable difficulty in solvents of high viscosity.

Table 9.2. Physical Properties of some Ionising Solvents

Solvent	Viscosity (millipoise)	Dielectric Constant	Autoionisation		Ionic Product
Water	10.08	78.5	$2H_2O$	$\rightleftharpoons H_3O^+ + OH^-$	10^{-14}
Ammonia	2.65	22	$2NH_3$	$\rightleftharpoons NH_4^+ + NH_2^-$	10^{-33}
Hydrogen Fluoride	2.4	84	$3HF$	$\rightleftharpoons H_2F^+ + HF_2^-$	$>10^{-14}$
Hydrogen Cyanide	2.0	107	$2HCN$	$\rightleftharpoons H_2CN^+ + CN^-$	10^{-19}
Sulphur dioxide	4.28	12.3	$2SO_2$	$\rightleftharpoons SO^{++} + SO_3^{--}$	10^{-13}

The dielectric constants of the ionising solvents in Table 9.2 can be properly appreciated against the dielectric constants of ~ 2 for common non-ionising solvents. It should be noted that solvents of high dielectric constants are generally highly polar, which characteristic leads, in turn, to association in the liquid state. The ionic products in the last column of Table 9.2 give an idea of the extent of autoionisation of the solvents.

We discuss below some of the characteristics of common non-aqueous solvents as also the nature of the reactions studied in these media.

9.3. LIQUID AMMONIA

Solvent character: Compared to water the effect of hydrogen bonding is less pronounced and the liquid is moderately associated. Its freezing point ($-77.7°C$) and boiling point ($-33.3°C$) are lower than those of water. The dielectric constant (22) is low compared to that of water (78.5). Ionic product (10^{-33}) is also smaller than that of water (10^{-14}). Liquid ammonia is therefore a weaker ionising solvent than water.

Table 9.3. Solubilities of some Salts and Organic Compounds in Water and liquid Ammonia:

Compound	H_2O	Liquid NH_3
NaCl	0.6 mole/100 gm (0°C)	0.22 mole/100 gm ($-1°C$)
NaI	1.07 ,,	0.88 ,,
Satd. C_nH_{2n+2}	insoluble	insoluble
Unsaturated hydrocarbons	insoluble	soluble or moderately soluble.

The above solubility differences appear to fall in line with the differences in dielectric constants of the two solvents. The general order of halide solubility in liquid ammonia is iodide > bromide > chloride > fluoride.

Solutions of metals: The alkalies and the alkaline earths are soluble in liquid ammonia providing a blue solution. In dilute solutions the metals are completely dissociated into metal ions and ammoniated electrons. The electrons are trapped in cavities in the solvent. The electrons are thus solvated. These solutions on evaporation leave behind the metals indicating that the electrons return to the parent ions. In moderately concentrated solution, however, the decomposition reaction

$$M + NH_3 = MNH_2 + \tfrac{1}{2}H_2$$
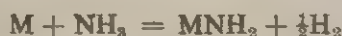
can occur photochemically or under the catalytic influence of transition metal ions. This behaviour is parallel to what the alkalies or the alkaline earths show in aqueous medium.

$$M + H_2O = MOH + \tfrac{1}{2}H_2$$

For further informations see section 14.1.2.

Reactions in Liquid Ammonia:

(1) *Neutralisation reactions:* Ammonium ion in liquid ammonia behaves as an acid and amide ion as a base. Imides and nitrides also behave as bases in this solvent. The following reactions therefore are examples of acid base neutralisation reactions:

$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$
$$NH_4Cl + KNH_2 = KCl + 2NH_3; 3NH_4I + BiN = BiI_3 + 4NH_3$$
$$2NH_4I + PbNH = PbI_2 + 3NH_3$$
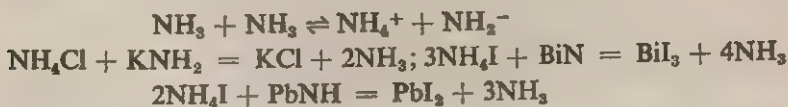
There is a close connection between water and liquid ammonia. The counterpart of amides and imides in liquid ammonia is the hydroxide in water. Nitrides in liquid ammonia are equivalent to oxides in water.

(2) *Precipitation reactions:* The precipitation reactions are exemplified by the following:

$$Zn(NO_3)_2 + 2NH_4I = ZnI_2 \downarrow + 2NH_4NO_3$$
$$Sr(NO_3)_2 + 2NH_4Br = SrBr_2 \downarrow + 2NH_4NO_3$$
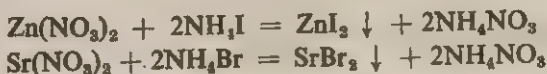
Zinc iodide and strontium bromide being insoluble in liquid ammonia are thrown out of solution. Note in aqueous medium both these compounds are highly soluble and no precipitation would occur.

It is quite interesting to note that although $AgNO_3$ and $NaCl$ react in water to precipitate $AgCl$ no such precipitation occurs in liquid ammonia. It is also fascinating to note that in this solvent $AgBr$ and $Ba(NO_3)_2$ interact to precipitate $BaBr_2$. Evidently complexation with the solvent itself does play a decisive role in deciding the nature of the precipitation. $AgCl$ remains soluble in the form of $[Ag(NH_3)_2]$ Cl.

(3) *Complex formation:* Zinc (II) amide, $Zn(NH_2)_2$, is sparingly soluble in liquid ammonia but dissolves readily in excess amide to form a complex ammonozincate.

$$Zn(NO_3)_2 + 2KNH_2 \rightleftharpoons Zn(NH_2)_2 + 2KNO_2$$
$$Zn(NH_2)_2 + 2KNH_2 \rightleftharpoons K_2[Zn(NH_2)_4]$$
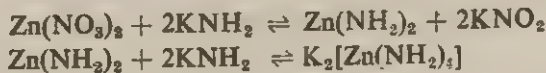
(4) *Oxidation-reduction reaction:* Solutions of the alkalies and the alkaline earths in liquid ammonia may act as electron donors (reducing agents) by releasing their labile valence electrons to electron acceptors (oxidising agents). The reaction of sodium with ammonium bromide is effectively an oxidation-reduction reaction:

$$2Na + 2NH_4Br \rightleftharpoons 2NaBr + 2NH_3 + H_2$$
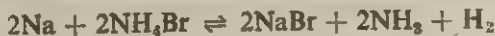
Na is oxidised to Na^+ and NH_4^+ reduced to $NH_3 + H_2$.

$$Na \rightarrow Na^+ + e; NH_4^+ \rightarrow NH_3 + H^+; 2H^+ + 2e \rightarrow H_2$$

(5) *Solvolysis reaction:* Just as in aqueous medium often a normal inorganic salt suffers hydrolysis to a basic salt, many inorganic salts react in liquid ammonia to produce ammono-basic compounds:

$$2PbI_2 + 3NH_3 \rightarrow Pb(NH_2)_2.Pb(NH_2)I + 3HI$$
$$HgCl_2 + NH_3 \rightarrow HgNH_2Cl + HCl$$

13
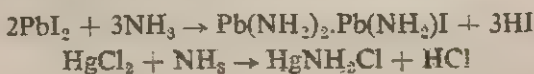
(6) *Amphoteric Behaviour in liquid ammonia*

$Mg(NH_2)_2$ and $Zn(NH_2)_2$ behave as amphoteric compounds in this solvent:

As Base : $2NH_4Cl + Mg(NH_2)_2 \rightarrow MgCl_2 + 4NH_3$

As Acid : $Mg(NH_2)_2 + 2NaNH_2 \rightarrow Na_2[Mg(NH_2)_4]$

As Base : $2NH_4Cl + Zn(NH_2)_2 \rightarrow ZnCl_2 + 4NH_3$

As Acid : $Zn(NH_2)_2 + 2NaNH_2 \rightarrow Na_2[Zn(NH_2)_4]$
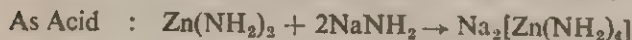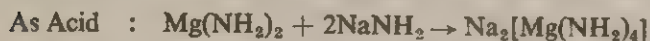
Compared to $NaNH_2$, $Mg(NH_2)_2$ and $Zn(NH_2)_2$ are weaker bases i.e. are acids in liquid ammonia.

The above 'acid' behaviours are comparable to the 'complexation reactions' mentioned earlier.

9.4. LIQUID HYDROGEN FLUORIDE

Solvent character: Anhydrous hydrogen fluoride is an associated liquid (B.P. 19.5°C) with a high dielectric constant (84). It is therefore a good solvent for ionising compounds. However anhydrous hydrogen fluoride is a highly reactive substance and thus many compounds decompose during dissolution.

Reactions in liquid Hydrogen Fluoride: The autoionisation reaction of HF is $3HF \rightleftharpoons H_2F^+ + HF_2^-$. Compounds like KF, NH_4F yield their simple ions first, which is followed by a further reaction of the fluoride ion with HF giving the anion HF_2^-. Thus these compounds behave as bases in this solvent.

$$KF \rightleftharpoons K^+ + F^-; HF + F^- \rightleftharpoons HF_2^-$$

A few other salts ($NaNO_3$, $AgNO_3$, Na_2SO_4, $NaClO_4$ etc) dissolve and form fairly stable conducting solutions. Note that these ions have nothing in common with HF, so that they behave as neutral ionic compounds in this medium and can give rise to precipitation reactions with AgF:

$$Na_2SO_4 + 2AgF \rightleftharpoons Ag_2SO_4 \downarrow + 2NaF$$
$$Ba(ClO_4)_2 + 2AgF = 2AgClO_4 \downarrow + BaF_2$$
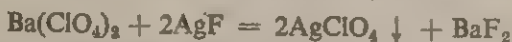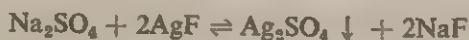
Unfortunately, many inorganic compounds are decomposed by this solvent. For example, metal chlorides give fluorides and hydrogen chloride which, being insoluble in HF, escape.

$$KCl + HF \rightarrow HCl \uparrow + KF \xrightarrow{HF} K^+ + HF_2^-$$

SbF_5 has been observed to behave as the strongest acid in liquid HF:

$$2HF + SbF_5 \rightleftharpoons H_2F^+ + SbF_6^-$$

This reaction proceeds with considerable evolution of heat. GeF_4, SnF_4, SeF_4, VF_5 etc exhibit definite but rather low acidic properties.

Aluminium (III) and chromium (III) fluorides show *amphoteric properties* in liquid HF.

As Acid : $3KHF_2 + AlF_3 \rightarrow 3HF + K_3AlF_6$

$(3HF_2^- + AlF_3 \rightarrow AlF_6^{3-} + 3HF)$

As Base : $Na_3AlF_6 + 3H(BF_4) \rightarrow AlF_3 + 3Na(BF_4) + 3HF$

(cf : $NaAlO_2 + H^+ + H_2O \rightarrow Al(OH)_3 + Na^+)$
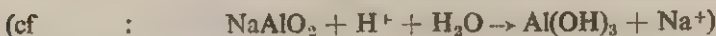
Often a solute adds an HF molecule and then breaks up into a cation and fluoride anion which in turn picks up another HF molecule and takes the form of HF_2^- (e.g.: CH_3COOH).

$$CH_3COOH + HF \rightleftharpoons CH_3COOH_2^+ + F^- \xrightarrow{\text{HF}} CH_3COOH_2^+ + HF_2^-$$
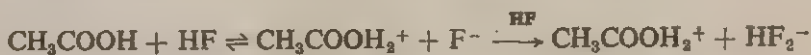
Weak protonic acids like CH_3COOH thus behave as bases in this medium.

Oxides and hydroxides react violently with liquid HF to form water and fluoride ion, the former reacting with HF to give HF_2^- and H_3O^+.

$$M_2O + 2HF = 2MF + H_2O; H_2O + HF \rightleftharpoons H_3O^+ + F^-$$
$$HF + F^- \rightleftharpoons HF_2^-$$
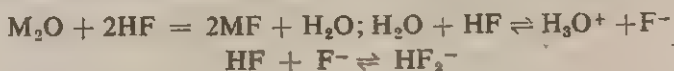
9.5. LIQUID SULPHUR DIOXIDE

Solvent character: Liquid sulphur dioxide boils at $-10.2°C$, freezes at $-75.5°C$ and has a low dielectric constant (12.3). It is therefore not a very good solvent for ionic substances but is a good one for many types of organic compounds. Metal oxides, sulphides, sulphates and hydroxides are practically insoluble in this solvent whereas metal sulphites, halides and thiocyanates are highly soluble. Compounds such as CCl_4, $SiCl_4$, $TiCl_4$, CS_2, $(CH_3)_2O$, C_6H_5Cl, alcohols, ketones, aldehydes are either very soluble or moderately soluble. It may be recalled Brönsted protonic concept will not apply in this aprotic solvent case, instead Lewis acid-base concept has to be applied.

Reactions in liquid Sulphur Dioxide: The autoionisation of liquid sulphur dioxide shows that the thionyl ion (SO^{2+}) should be an acid and the sulphite ion (SO_3^{2-}) should be the base:

$$2SO_2 \rightleftharpoons SO^{2+} + SO_3^{2-}$$

Thus the reaction of thionyl chloride and caesium sulphite is an *acid base reaction* in this solvent. The reaction can be followed conductometrically with a break at 1:1 ratio of $SOCl_2$ and Cs_2SO_3.

$$SOCl_2 + Cs_2SO_3 \rightleftharpoons 2CsCl + 2SO_2$$
$$\text{acid} \quad \text{base} \quad \text{salt} \quad \text{solvent}$$
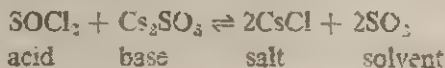
The above reaction is comparable to the following reaction in aqueous medium:

$$HCl + CsOH \longrightarrow CsCl + H_2O$$
$$\text{acid} \quad \text{base} \quad \text{salt} \quad \text{solvent}$$
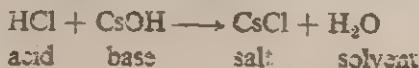
Two soluble ionic substances may lead to *precipitation reactions* as shown by the following reactions:

$$BaI_2 + Zn(CNS)_2 \rightleftharpoons Ba(CNS)_2 \downarrow + ZnI_2$$

$$AlCl_3 + 3NaI \rightleftharpoons 3NaCl \downarrow + AlI_3$$
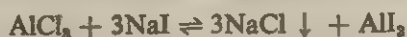
Complexation reactions are also observed in this medium. For instance, aluminium chloride and caesium sulphite first react to precipitate $Al_2(SO_3)_3$, which dissolves in excess caesium sulphite to form a soluble sulphite complex of aluminium.

$$2AlCl_3 + 3Cs_2SO_3 \rightleftharpoons Al_2(SO_3)_3 + 6CsCl$$

$$Al_2(SO_3)_3 + 3Cs_2SO_3 \rightleftharpoons 2Cs_3[Al(SO_3)_3]$$
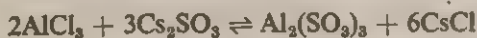
Oxidation-reduction reactions have also been carried out in this solvent. The oxidation of potassium iodide by antimony (V) chloride proceeds quantitatively:

$$6KI + 3SbCl_5 \rightarrow 2K_3[SbCl_6] + SbCl_3 + 3I_2$$

Solvolysis of phosphorus pentachloride occurs in this solvent.

$$PCl_5 + SO_2 \rightleftharpoons POCl_3 + SOCl_2$$

$$NbCl_5 + SO_2 \rightarrow NbOCl_3 + SOCl_2$$

Amphoteric Behaviour: Solutions of $AlCl_3$ and $[(CH_3)_4N]_2SO_3$ in liquid SO_2 precipitate $Al_2(SO_3)_3$. This dissolves in excess of the sulphite base from which solution $Al_2(SO_3)_3$ can be reprecipitated by the addition of the acid $SOCl_2$;

$$2AlCl_3 + 3[(CH_3)_4N]_2SO_3 \rightarrow Al_2(SO_3)_3 + 6[(CH_3)_4N]Cl$$

$$Al_2(SO_3)_3 + 3[(CH_3)_4N]_2SO_3 \rightarrow 2[(CH_3)_4N]_3Al(SO_3)_3$$

$$2[(CH_3)_4N]_3Al(SO_3)_3 + 3SOCl_2 \rightarrow 6[(CH_3)_4N]Cl + 6SO_2 + Al_2(SO_3)_3$$
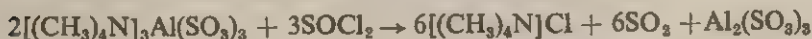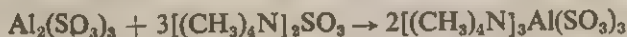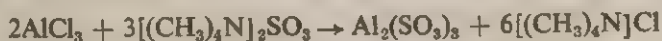
9.6. LIQUID HYDROGEN CYANIDE

Although this liquid has a high dielectric constant (107), its solvating properties are inferior to those of water. Its poisonous nature has seriously limited studies in this solvent. The autoionisation reaction is:

$$HCN + HCN \rightleftharpoons H_2CN^+ + CN^-$$
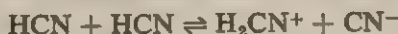
Substances releasing protons (e.g.: sulphuric acid) should act as acids and those producing cyanide (e.g.: triethyl ammonium cyanide) should function as bases. Precipitation and complexation reactions will be of the following forms:

$$FeCl_3 + 3[(C_2H_5)_3NH]CN \rightleftharpoons Fe(CN)_3 \downarrow + 3[(C_2H_5)_3NH]Cl$$

$$Fe(CN)_3 + 3[(C_2H_5)_3NH]CN \rightleftharpoons [(C_2H_5)_3NH]_3[Fe(CN)_6]$$
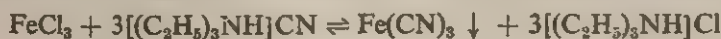
9.7. LIQUID HYDROGEN SULPHIDE

This solvent (B.P. $-61°C$) has a low dielectric constant (10.2). The autoionisation reaction is:

$$2H_2S \rightleftharpoons H_3S^+ + SH^-$$

Solutes yielding hydrogen ion on dissolution would behave as acids and those yielding SH^- ions will function as bases. Thus neutralisation reactions between acids (eg: HCl, HBr, CH_3COOH etc) and bases (e.g.: trimethyl ammonium sulphide $[(C_2H_5)_3NH]SH$ can be carried out. Solvolysis also occurs in many instances, for example, Hg_2Cl_2 react with H_2S to give $Hg_2(SH)_2$, and $AsCl_3$ to form As_2S_3.

9.8. SOME MORE NON-AQUEOUS SOLVENTS

Instead of going into the details of inorganic reactions in many other non-aqueous solvents we only cite a few autoionisation reactions of some more solvent systems. These autoionisation reactions are enough to make one guess the course and type of reactions to be expected in such systems.

Table 9.4. Properties of some more Solvents

Solvent		Autoionisation reaction	Dielectric Constant
Phosphorus Oxytrichloride	$POCl_3$	$\rightleftharpoons POCl_2^+ + Cl^-$	13.0
Selenium Oxychloride	$SeOCl_2.$	$\rightleftharpoons SeOCl^+ + Cl^-$	46.2
Carbonyl Chloride.	$COCl_2$	$\rightleftharpoons COCl^+ + Cl^-$	4.34
Acetyl Chloride	CH_3COCl	$\rightleftharpoons CH_3CO^+ + Cl^-$	16.9
Acetyl Bromide	CH_3COBr	$\rightleftharpoons CH_3CO^+ + Br^-$	16.5
Ethyl Acetate	$CH_3COOC_2H_5$	$\rightleftharpoons CH_3CO^+ + OC_2H_5^-$	6.0
Nitromethane	CH_3NO_2	$\rightleftharpoons CH_2NO_2^- + H^+$	38.6
Acetic Acid	CH_3COOH	$\rightleftharpoons CH_3COO^- + H^+$	6
Acetonitrile	CH_3CN	$\rightleftharpoons CH_2CN^- + H^+$	36

STUDY QUESTIONS

1. Aniline cannot be titrated in aqueous medium with an acid but the titration can be done in glacial acetic acid. Comment.

2. What are the principal species expected in solutions of the following solutes in water, anhydrous H_2SO_4 and liquid ammonia- NaOH, SO_3, $(NH_4)_2SO_4$ and H_2O.

3. Ammonia is a base according to Lowry-Brönsted concept and also according to Lewis theory. Comment. Discuss some reactions in this solvent in support of the two concepts.

4. The reaction HCl (aq) + KOH (aq) → KCl (aq) + H_2O is neutralisation according to (a) Lowry-Brönsted concept (b) Lewis theory and (c) Solvent system concept. Comment. Take two non-aqueous solvents and discuss the reaction between HCl and KOH.

5. Water has a much higher boiling point than ammonia. Water is a better solvent for salts but a poorer one for organic compounds. Attempt to find a link between these two statements.

6. Explain: (a) A liquid ammonia solution of phenolphthalein is colourless but becomes red on addition of KNH_2 (b) Liquid ammonia becomes quite conducting on addition of NH_4Br (c) Liquid $COCl_2$ has a low conductivity which is increased on addition of $AlCl_3$. The resulting solution reacts with metals with evolution of CO.

7. Why is it that in a given solvent, acids and bases are usually soluble but amphoteric compounds are precipitated?

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Coordination Chemistry

10.1. INTRODUCTION

Tassaert made the beginning in 1798 with an orange coloured compound, $CoCl_3.6NH_3$, obtained on standing an ammoniacal solution of cobalt (II) chloride. This same compound is now easily obtained in a pure state and in high yield by air-oxidation of ammoniacal cobalt (II) chloride in the presence of active charcoal as a catalyst. The structures of such compounds were the subject of prolonged controversies between two famous adversaries of the late nineteenth century, Jorgensen and Werner. Werner finally solved the mysteries and brought order into the area by announcing his famous coordination theory.

In his coordination theory Werner introduced two great ideas: (1) In a coordination complex a metal ion is engaged in strong binding with a certain number of neutral and/or anionic groups in the first sphere of attraction, now called the *coordination zone* or *sphere:* (2) The metal ion is surrounded by the neutral and/or anionic groups in the coordination zone in a definite geometrical arrangement.

Werner argued that metal ions possessed two kinds of valence: a *primary valence* and a *secondary valence.* Primary valence was satisfied by requisite number of anions or negative groups being present inside and/or outside the coordination sphere. Secondary valence indicated the capacity of the metal ion to accommodate certain number of groups around itself in the first sphere of attraction. *Primary valence is now equated with the oxidation state and the secondary valence with the coordination number of the metal ion.*

Werner's ideas were supported by experimental findings on many compounds. It was shown by a large number of simple metathetic reactions on $CoCl_3.6NH_3$ in aqueous solution that changes were forced only on the chloride part leaving cobalt and the six NH_3 groups intact.

Werner realised that $CoCl_3.6NH_3$ should better be represented as a strongly bound unit $[Co(NH_3)_6]^{3+}$, leaving the three chloride units as anions outside the

square bracket. The unit within the square bracket was recognised as a complex entity, formed as a result of coordination of the neutral NH_3 molecules to the Co^{3+} cation, both these being capable of independent existence. That such a formulation was indeed correct was amply verified by conductance measurements
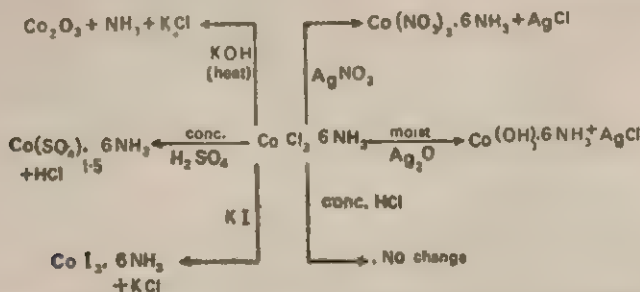
Chart 10-I. Werner's metathetic reactions on $CoCl_3.6NH_3$.

$(\Lambda_{1024} = 432$ ohms^{-1} cm^2 mole^{-1}), the value being close to those of authentic tri-univalent ions ($CeCl_3$, 408 and $K_3Fe(CN)_6$, 435 ohms^{-1} cm^2 mole^{-1}). Werner named the zone within the square bracket as the first sphere of attraction, the anions being held in a second sphere of attraction.

According to Werner the geometrical arrangement around cobalt (III) was octahedral and hence there should be six groups around cobalt (III). The primary valence of $+3$ of cobalt (III) in $[Co(NH_3)_6]Cl_3$ is satisfied by the three chloride ions while the secondary valence is satisfied by the six NH_3 groups. Werner formulated $CoCl_3.5NH_3$ as $[CoCl(NH_3)_5]Cl_2$ indicating once again that the primary valence of cobalt (III) is satisfied by one Cl^- inside the coordination zone and two Cl^- outside the coordination zone. In accordance with this formulation the compound is a bi-univalent electrolyte. The compound $CoCl_3.3NH_3$ was given a non-electrolyte structure $[CoCl_3(NH_3)_3]$.

It is now quite amusing to note the way Jorgensen tried to explain the structures of the cobalt (III) ammines. Following the structure of ethylenediamine chloride (a), Jorgensen represented the cobalt (III) ammines with chains of different lengths. He thought that the valences of cobalt in these
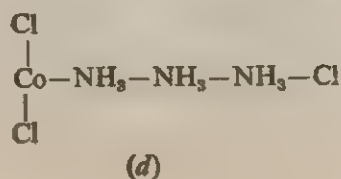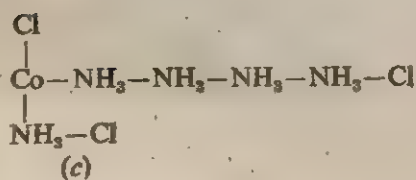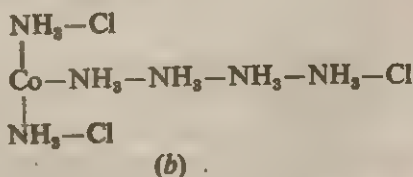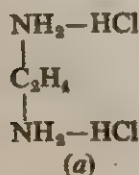
compounds were different and therefore stabilised chains of different lengths. Since in $CoCl_3.6NH_3$ (b) all the three chlorines were some distance away from cobalt these were, according to Jorgensen, readily precipitated by silver nitrate while in $CoCl_3.5NH_3$ (c) two chlorines were expected to be readily precipitated. Such reasoning would predict that for the-then-unsynthesised $CoCl_3.3NH_3$ (d) only one chlorine would be readily precipitated. This compound could not be prepared by Jorgensen but its iridium (III) analogue, $IrCl_3.3NH_3$, was prepared and it failed to give any precipitate with $AgNO_3$. This showed that all the three chlorines were strongly bound and that Jorgensen could not be right.

Jorgensen's problem was that he refused to think of these complicated molecules in any other way outside the chain theory. But characteristic of a genius Alfred Werner brought in a bundle of fresh thoughts in this area and that made all the difference.

Alfred Werner played such a monolithic pivotal role in the development of coordination chemistry that the subject is now synonymous with his name. His researches on the coordination chemistry of metal ammines are now classics. Metal ammines and related complexes are often lovingly called Werner complexes.

10.2. DEFINITIONS: COMPLEX, LIGAND AND COORDINATION NUMBER

A metal ion (whether it is positively charged, neutral or even negatively charged) may combine with neutral molecules or anions to give a new reasonably identifiable entity called a *complex*. The groups that surround the metal ion in a complex are called *ligands*. The ligands are arranged around the metal ion

$$M^{n+} + xL \rightleftharpoons [ML_x]^{n+}$$

inside the first sphere of attraction in preferred geometries. The number of the ligands bound around a metal ion is called the *coordination number* of the metal ion. In the above reaction a metal ion M^{n+} reacts with x moles of a neutral ligand L (each capable of taking one coordination position) to form a complex $[ML_x]^{n+}$. Here x represents the coordination number. In $[Co(NH_3)_6]Cl_3$, Co^{3+} has a coordination number six.

It will now be proper to discuss any difference between a double salt and a complex salt. A double salt such as $KAl(SO_4)_2.12H_2O$ or $3CsCl.CoCl_2$ is so very dissociated into its component ions (in, say, water) that there does not exist any reasonably identifiable complex entity. On the other hand, in complexes $CoCl_3.6NH_3$ or $CuCl_2.4NH_3$ we have identifiable complex entities $[Co(NH_3)_6]^{3+}$ or $[Cu(NH_3)_4]^{2+}$. A very weak complex wholly dissociates into its component ions. Therefore in a suitable solvent a double salt breaks down into component ions, which can be detected by the usual tests of these ions. A stable complex ion, obviously, will not respond to the tests of its component units.

10.3. COMPLEXATION—A DONOR-ACCEPTOR INTERACTION

Structure determinations have shown that most polar ligand molecules are so oriented in a complex that one unshared pair of electrons points directly to

the metal ion. The ligand is a donor of electrons and the metal ion an acceptor. However this statement will be profoundly modified when the metal ion is in a low oxidation state and when the ligand possesses acceptor orbitals in addition to donor orbitals.

10.4. CLASSIFICATIONS OF LIGANDS

Based on donor and acceptor properties ligands may be of the following types:

Ligands

(1) With one (or more) lone pair (s) of electrons

(2) Without a lone pair of electrons but with π-bonding electrons e.g.: ethylene, benzene, cyclopentadienyl ion.

(a) No vacant orbitals to receive back donated electrons from metal

e.g.: H_2O, NH_3, F^-

(b) Vacant orbitals that can be used to receive back donated π electrons from the low oxidation state metal

e.g.: PR_3, CN^-, CO
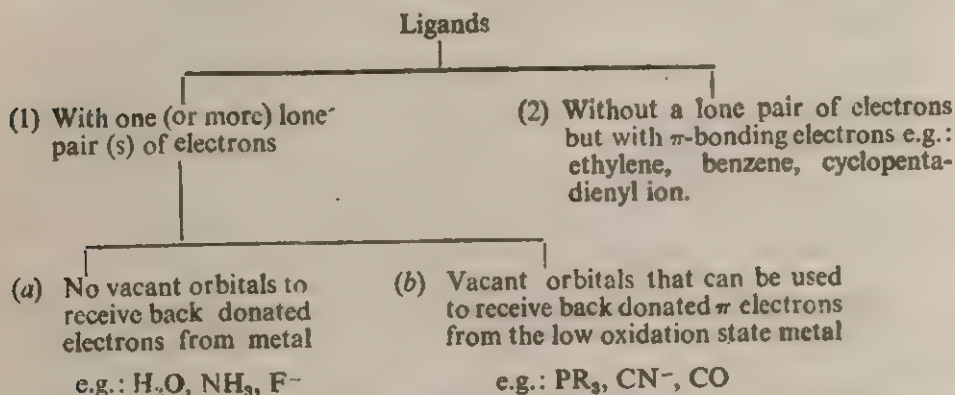
Ligands may also be classified according as the number of coordination positions they occupy around the metal ion (Table 10.1). A ligand having only one lone pair of electrons can only be bonded to a metal ion at just one stereochemical point, that is, it occupies one coordination position only. This is called a unidentate or a monodentate ligand. When the ligand can occupy two positions around the metal ion it is bidentate; with three, four, five or six such links the ligands are called tri (ter) dentate, quadri (tetra) dentate, penta (quinque) dentate or sexa (hexa) dentate respectively. Some authors prefer to classify ligands according to the number of donor atoms they can offer to metal ions. Thus, when a ligand has two atoms which can *simultaneously* serve as donors it is called bidentate and so on. It follows that a bidentate ligand has to have two lone pairs, a tridentate

Table 10.1. Some Monodentate and Polydentate Ligands
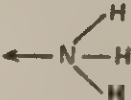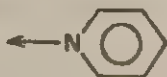
Ligand type	Name	Formula
Monodentate	Ammonia	
	Pyridine	

Table 10.1. (Continued)
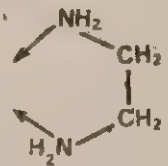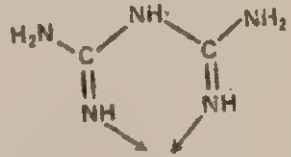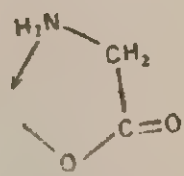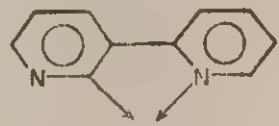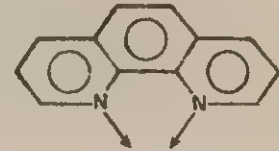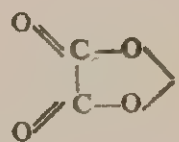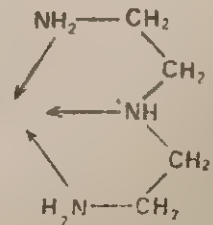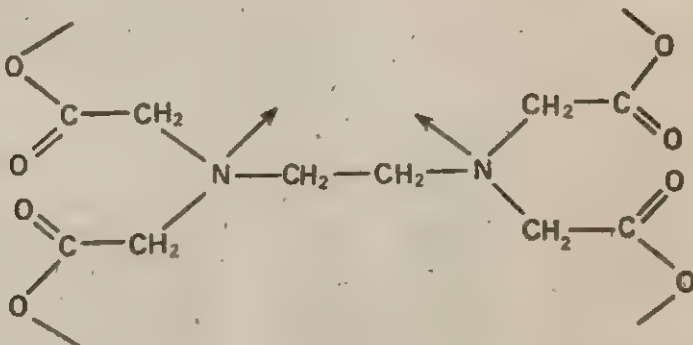
Ligand type	Name	Formula
	ethylenediamine (en)	
	Biguanide (BigH)	
	Glycinate ion (gly)	
Bidentate	Dipyridyl (dipy)	
	o-Phenanthroline (o-phen)	
	Oxalate ion (ox)	
Tridentate (Terdentate)	Diethylenetriamine (dien)	

Tabld 10.1. (Continued)

Ligand type	Name	Formula
Tridentate (Terdentate)	Iminodiacetate ion (IDA)	
	Triethylenetetramine	
Quadridentate (Tetradentate)	Ethylene bis (salicylaldimine) anion	
Quinquedentate (Pentadentate)	ethylenediamine triacetic acid anion	

Table 10.1. (Continued)

Ligand type	Name	Formula
Sexadentate (Hexadentate)	ethylenediamine tetra-acetic acid anion (EDTA)	

three lone pairs and so on. The polydenate ligands may be further subdivided according to the nature of their donor centres. Thus ethylenediamine is a bidentate ligand with two neutral donors (N) whereas oxalate ion is bidentate with two acidic (anionic) donors (O^-). Glycinate ion is again a bidentate with one neutral donor (N) and an acidic donor (O^-). Such discussions may be extended to other poly-dentates as well.

A *chelating ligand* is one that contains two or more donor centres so disposed that they can simultaneously occupy more than one position around the same metal ion in the first sphere of coordination. The resulting complexes are called metal chelates. Thus all polydentate ligands, when bonded to the same metal ion, are also chelating ligands. A chelating ligand must possess two or more lone pairs such distance apart that it may form suitable strain-free rings at the metal ion. Too small-sized and too large-sized rings are unsuitable for stable binding. Usual strain-free rings are 5— or 6— membered ones. 4— and 7— membered chelate rings are also known but are less stable than 5— or 6— membered ones.

A *bridging ligand* is one that can simultaneously bond itself to more than one metal ion. OH^-, Cl^-, NH_2^- etc can function as monodentate and also as bridging ligands. A bridging ligand must have at least two lone pairs so that it can get linked to at least two metal ions. A polydentate ligand may function both as a chelating ligand and as a bridging ligand. Note that OH^-, Cl^- or NH_2^- cannot serve as chelating ligands because the angle between the lone pairs would not allow them to span adjacent coordination positions of one and the same metal ion. Hydrazine, NH_2-NH_2, can serve as a monodentate and as a bridging ligand but not as a chelating ligand because a 3-membered ring will be too strained to be stable (cf. 18-I).

A polydentate ligand may not bring into play all its donor centres while getting coordinated to a metal ion. Thus ethylenediamine tetraacetic acid, usually

a formidable sexadentate ligand, is also known to function as a quinquedentate ligand in M[Cr(OH)(EDTA)] or in M[Co(Br)(EDTA)] (M = bipositive cation) or as a quadridentate ligand in [Pd(H_2EDTA)]. Iminodiacetate anion, usually a tridentate ligand, functions as a bidentate one in the mixed chelate [Co(IDA)(BigH)$_2$]$^+$. These behaviours are manifestations of *flexidentate* character of polydentate ligands.

A flexidentate ligand is one that can chelate a metal ion in more than one way. For example cysteine, $HS-CH_2-CH(NH_2)-COOH$ can function as a tridentate (SNO) and as a bidentate in three ways again (SN; NO; SO).

Currently it has been brought to light that very simple molecules like N_2 and O_2 can also act as coordinating ligands. N_2 has a triple bond and a lone pair on each of the two nitrogens. Hence it can function both as a monodentate as well as a bridging ligand eg: [Ru(NH$_3$)$_5$(N$_2$)]$^{2+}$, [(NH$_3$)$_5$ Ru←(N$_2$)→Ru(NH$_3$)$_5$]$^{4+}$ Dioxygen (O$_2$) usually takes part in complex reactions as a bidentate (obviously highly strained form) ligand eg: [Ir(PPh$_3$)$_2$(CO) (Cl) (O$_2$)]. Considerable lengthening of the O−O distance (1.3 to 1.63A) occurs (cf. O$_2$ ~ 1.32A).

Compared to monodentate ligands, chelating ligands form complexes of greater stability. Greater stability indicates smaller dissociation of the complex into its components in a particular solvent.

10.5. COORDINATION NUMBER AND STEREOCHEMISTRY

Since a complex is the result of an interaction between a metal ion and a certain number of ligands, it follows that the qualities of the two reactants ultimately dictate the coordination number of the metal ion and the geometry, that is, the stereochemistry of the complex.

While it is necessary to point out that the coordination number and the resulting stereochemistry are not always predictable certain broad features, however, may be outlined.

1. *Since an attraction between a metal ion and dipolar molecules or anions is involved, the coordination number will tend to be as large as possible.*

2. *The arrangement of the coordinated ligands must be such that it minimises the electrostatic repulsion between ligands.*

An ML$_2$ type complex therefore should be linear for such a geometry maximises the L−L distance and hence minimises the repulsion between the two L groups. Similarly an ML$_3$ complex should have the three L ligands at the vertices of an equilateral triangle. For a coordination number four (ML$_4$ complex) the four L groups may be placed at the corners of a regular tetrahedron or at the corners of a square plane, both stereochemistries assuming minimisation of repulsive forces. Likewise a coordination number five admits of two stereochemistries, a square pyramid and a trigonal bipyramid An octahedron, a hexagon or a trigonal prism satisfies a coordination number six but in reality the octahedron appears to be the preferred one. These stereochemistries are illustrated below (Fig. 10.1). Coordination numbers seven and eight are known but are scarce and will not be discussed. Table 10.2 describes some stereochemistries with examples.
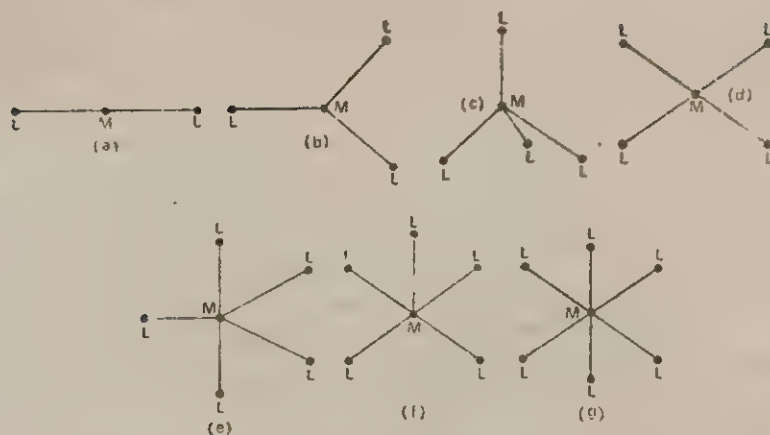
FIG. 10.1. Coordination numbers and stereochemistries (*a*) linear ML_2 (*b*) equilateral triangular ML_3 (*c*) tetrahedral ML_4 (*d*) square planar ML_4 (*e*) trigonal bipyramidal ML_5 (*f*) square pyramidal ML_5 and (*g*) octahedral ML_6.

10.5.1. Complexes with Coordination Number 2 or 3: When silver salts dissolve in ammonia the complex $[H_3N \rightarrow Ag \leftarrow NH_3]^+$ is produced. This has a linear stereochemistry. Other complexes of coordination number two are mostly restricted to copper (I), silver (I), gold (I) and mercury (II). Examples of coordination number three are scanty. The $[HgI_3]^-$ anion perhaps is the best investigated. In this anion the iodide ions are arranged at the corners of a slightly distorted equilateral triangle with the mercury (II) at its centre. Two other examples are chloro bis (thiourea) copper (I) and tris (triphenylphosphine) platinum (O). Equilateral triangular coordination has been verified by X-ray crystallographic studies in these cases. Several complexes apparently with coordination number three e.g.: $(R_3P)_2$ CuI, (dipy)CuI etc. are in reality halo-bridged dimers, thus raising the coordination number effectively to four.

Table 10.2. Examples of different complexes showing different Coordination Numbers and Stereochemistries

Coordination Number	Examples	Stereochemistry
2	$[Ag(NH_3)_2]^+$, $[CuCl_2]^-$, $[Hg(CN)_2]$	Linear
3	$[HgI_3]^-$, $[CuCl(tu)_2]$	Distorted equilateral triangle
4	$[CoCl_4]^{2-}$, $[NiCl_2(PPh_3)_2]$ $[NiCl_2(OPPh_3)_2]$	Tetrahedral
4	$[Pt(NH_3)_4]^{2+}$, $[Cu(en)_2]^{2+}$ $[Ni(DMG)_2]$, $[PtCl_2(PPh_3)_2]$	Square planar

Table 10.2. (Continued)

Coordination Number	Examples	Stereochemistry
5	[VO(acac)₂]	Square pyramidal
5	[Cu(dipy)₂I]I	Trigonal bipyramidal
6	[Co(NH₃)₆]²⁺, [Cr(en)₃]³⁺	Octahedral

OPPh₃ = triphenylphosphine oxide; en = ethylenediamine;
DMG = dimethylglyoximate ion; acac = acetylacetonate ion;
dipy = dipyridyl; tu = thiourea

10.5.2. Complexes with Coordination Number 4: Weak donor ligands such as Cl⁻, PPh₃, OPPh₃ can enforce only a tetrahedral stereochemistry with the ligand-metal-ligand angle around 109°. On the contrary all strong ligand complexes with coordination number four force a square planar stereochemistry with the ligand-metal-ligand angle around 90°. Common examples of tetrahedral complexes are the blue coloured [CoCl₄]²⁻ (often encountered in practical class on adding enough HCl to the pink aqueous cobalt (II) chloride), [CuCl₄]²⁻, [NiCl₄]²⁻, [NiCl₂(PPh₃)₂] etc. Square planar stereochemistry is known for bis (dimethylglyoximato) nickel (II), bis (ethylenediamine) copper (II), bis (biguanide) nickel (II), bis (biguanide) copper (II), dichloro diammine platinum (II) etc.

10.5.3. Complexes with Coordination Number 5: This coordination number has been extensively investigated in recent times. A large number of nickel (II) and cobalt (II) complexes with Schiff bases and also with trivalent phosphorus ligands

Trigonal bipyramidal iodobis (dipyridyl) copper (II)

(10-I)

Square pyramidal bis (acetylacetonato) oxovanadium (IV)

(10-II)
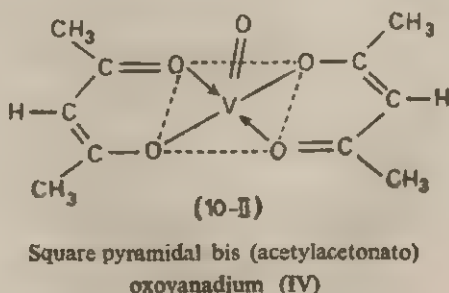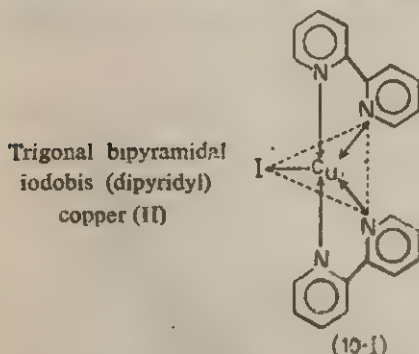
are known. Several oxovanadium (IV) complexes are known with square pyramidal geometry. Fe(CO)₅, Mn(CO)₅⁻, (R₃P)Fe(CO)₄ have trigonal bipyramidal configurations. [NiBr₃(P(C₂H₅)₃)₂] and [Cu(dipy)₂I]I (10-I) also possess trigonal bipyramidal structures. Bis (acetylacetonato) oxovanadium (IV) (10-II) possesses a square pyramidal structure.

10.5.4. Complexes with Coordination Number 6 : Although this commonest coordination number conforms to octahedral geometry, limited examples are known (section 10.10) where trigonal prismatic stereochemistry has been established. It may be noted, however, that depending on the nature of the coordinating ligands, there might occur considerable distortion of the octahedral geometry. The octahedron suffers tetragonal distortion on pulling out two oppositely facing ligands (say, the two B's in trans Ma_4B_2). Such tetragonal distortion may finally lead to a square planar structure.

It appears from accumulated experimental results that the frequency of occurrence of coordination numbers for some common ions of the first transition series is roughly as given below:

Oxovanadium (IV) : 6(octahedral) $\simeq$ 5(square pyramidal), others rare
Chromium (III)   : 6(octahedral) $\gg$ 5, others very rare
Iron (III)   : 6(octahedral) $>$ 4(tetrahedral)
Cobalt (II)   : 6(octahedral) $>$ 4(tetrahedral) $> 5 >$ 4(planar)
Cobalt (III)   : 6(octahedral) $\gg$ 5, others unknown
Nickel (II)   : 6(octahedral) $>$ 4(planar) $\simeq$ 4(tetrahedral)
Copper (II)   : 6(octahedral) $\simeq 5 \simeq$ 4(planar) $\sim$ 4(tetrahedral)

There is thus no fixed coordination number or stereochemistry for any given ion. A particular stereochemistry may be enforced by the donor strength of the ligand, steric requirements, of the ligand, the size and charge of the metal ion etc.

10.6. NOMENCLATURE OF COORDINATION COMPLEXES

The International Union of Pure and Applied Chemistry has recommended in 1960 elaborate rules for naming complicated coordination complexes.

A. Order of listing ions: The cation is named first and then the anion.

B. Naming of the coordinated groups: (a) Neutral groups are generally named by the name of the molecules. Exceptions are H_2O (aquo), NH_3 (ammine), CO (carbonyl), NO (nitrosyl).

(b) Negative ligands (but not anions) are named with an ending —o after the stem-name of the anion: F^-(fluoro-), Cl^-(chloro-), CN^-(cyano), O^{2-}(oxo), OH^-(hydroxo), CH_3COO^-(acetato), HON $=$ $C(CH_3)C(CH_3)$ $=$ NO^-(dimethyl-glyoximato), $\underline{S}CN^-$(thiocyanato), $\underline{N}CS^-$(isothiocyanato), NO_2^-(nitro), $O\underline{N}O^-$(nitrito) etc.

For well-known ambidentate ligands naming is such that it provides an indication as to the donor atom attached to the ligand. Thus when the sulphur end of SCN^- is coordinated it is to be read as *thiocyanato*. When the nitrogen is the donor the nomenclature is *isothiocyanato*. Thus N-coordinated NO_2^- is *nitro while* O-bonded $O\underline{N}O$ is nitrito.

C. Naming of mononuclear complex ions:

(a) If the compound is ionic, the complex cation is mentioned first.

(b) For a cationic or neutral complex, the ligands are listed starting with the negative ones, then the central metal ion is named with a roman numeral in parenthesis stating its valence. When several such ligands appear in the complex

14

zone they are listed alphabetically. In 1970 it was suggested that the neutral ligands be named first and then the anionic ligands. However chemists are using both the 1960 and 1970 rules.

(c) For an anionic complex, the suffix -ate is attached to the name of the central metal ion again being followed by the appropriate roman numeral.

(d) The number of each kind of ligand is specified using prefixes di-, tri-, tetra-, penta- and hexa-. When the organic ligands are polysyllabic and themselves contain prefixes mono-, di-, tri, etc they are written within parentheses and the number of such ligands is indicated by prefixes bis, tris, tetrakis-, pentakis- and hexakis-. The following examples illustrate these rules:

$[Co(NH_2)_6]Cl_3$	Hexammine cobalt (III) chloride
$[Pt(NH_3)_2Cl_2]$	Dichlorodiammine platinum (II)
	Diammine dichloro platinum (II)
$K_3[Al(C_2O_4)_3]$	Potassium trioxalatoaluminate (III)
$[Pt(en)(NH_3)_2(NO_2)Cl]SO_4$	Chloronitrodiammine (ethylenediamine) platinum (IV) sulphate
	Diammine (ethylenediamine) chloro nitro platinum (IV) sulphate
$[Co(en)_3]Cl_3$	Tris (ethylenediamine) cobalt (III) chloride
$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate (II)
$[VO(acac)_2]$	Bis (acetylacetonato) oxovanadium (IV)
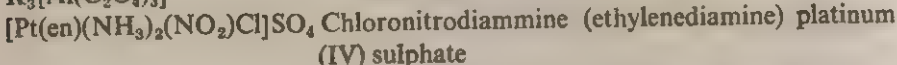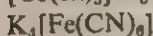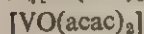
D. Bridging groups: Groups which hold two coordination centres carry a prefix μ.
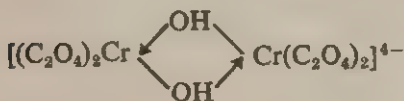
$[(C_2O_4)_2Cr \overset{OH}{\underset{OH}{<}} Cr(C_2O_4)_2]^{4-}$	Bis (oxalato) chromiate (III) μ-dihydroxo bis (oxalato) chromiate (III).
$[(en)_2Co \overset{NH}{\underset{OH}{<}} Co(en)_2]^{3+}$	Bis (ethylenediamine) cobalt (III) μ-imido-μ-hydroxo bis (ethylenediamine) cobalt (III).
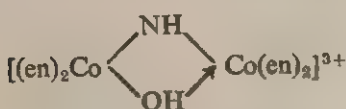
E. Geometric isomers and optical isomers: Cis- and trans-prefixes are added depending on the mode of the attachment of the coordinating groups inside the first sphere. d- and l-prefixes are added to indicate the nature of the optical activity of the optical isomers.

10.7. INNER METALLIC COMPLEXES

Cobalt (III) shows consistently a coordination number six. For example in tris (ethylenediamine) cobalt (III) chloride complex three molecules of bidentate ethylenediamine are required to satisfy the coordination number. The charge on cobalt (III) is taken care of by the three chloride ions. Instead of taking the ethy-

lenediamine if we choose the glycinate ion as a ligand we will get [Co(giv)₃]° in which both the coordination number and the charge on the cation are internally compensated by the ligands. *Such complexes where the coordination number and charge of the cation are internally compensated either partially or fully by the co-ordinated groups are called inner metallic complexes or simply inner complexes.* Inner complexes are sparingly soluble in aqueous medium but are sometimes soluble in organic solvents. Such complexes have played significant roles in devising suitable analytical procedures for estimation and identification of metal ions (section 10.16). For an explanation of the insolubility of non-electrolyte complexes in water and of their solubility in non-aqueous solvents see page 190 and 9.2)

In an inner complexing ligand both a neutral donor centre and an anionic donor centre are present suitable distance apart so as to make a 5 or 6 membered ring at the metal ion. When the number of such inner complexing ligands inside the coordination sphere of a complex satisfies both the coordination number and the charge on the metal ion, the resulting complex is a non-electrolyte e.g.

(10-III) (10-IV)

(10-V) (10-VI)
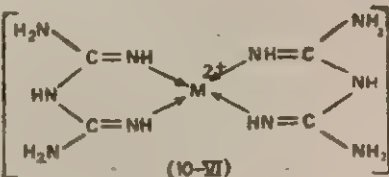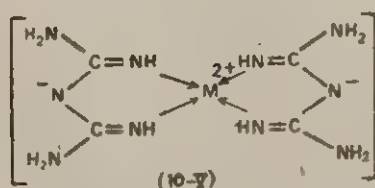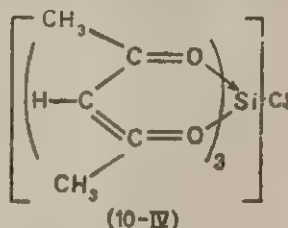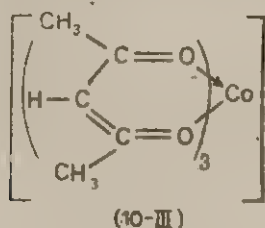
[Co(gly)₃], [Co(acac)₃] (10-III), [Cr(acac)₃] etc. These complexes are termed inner metallic complexes of the first order. On the contrary, when the charge and the coordination number of the metal ion are not fully satisfied at the same time by the ligands the result is an ionic species called an inner metallic complex of the second order. For instance silicon (IV) has a coordination number six but a charge +4. Hence in [Si(acac)₃]Cl (10-IV), the three 'acac' ligands satisfy only the coordination number but not the charge. A chloride ion in the second sphere is needed for charge neutralisation. Further examples are Na[Co^{II}(acac)₃], [B(acac)₂] [FeCl₄] etc. Inner complex salts of the second order may also be formed when the coordination sphere is only partially occupied by an inner metallic ligand. Thus, acetylacetone reacts with sodium cobaltinitrite to provide Na[Co(NO₂)₂(acac)₂]. A *third order complex* was described by Ray. Biguanide, NH₂—C—NH—C—NH₂ functions as a monobasic, bidentate ligand. Recent
   ‖   ‖
   NH NH

structural studies have revealed that the ligand coordinates symmetrically through the two $=NH$ groups. In the anhydrobases (10-V) deprotonation of the nitrogen in the

$$C \overset{NH}{\diagup \diagdown} C$$
$$\parallel \qquad \parallel$$

segment occurs, thus exhibiting the character of inner metallic complexes of the first order. These neutral first order complexes on careful treatment with acids leads to soluble salts (10-VI) as a result of the protonation of the negative nitrogen of the

$$C \overset{N^-}{\diagup \diagdown} C$$
$$\parallel \qquad \parallel$$

segment. Conversion of a nonelectrolyte first order complex into a cationic complex due to protonation of some negative centre of the ligand gives a third order complex. Thus [Cu(C₂N₃H₆)₂] (rose) is first order inner metallic complex which changes to third order [Cu (C₂N₅H₇)₂]Cl₂ (rose) on neutralisation with dilute HCl.

10.8. ORGANIC SEQUESTERING AGENTS

When an organic coordinating ligand forms a stable water-soluble metal chelate, the ligand is called an organic sequestering agent and the metal ion is said to be sequestered (or masked). For example, 8-hydroxyquinoline (oxin H) precipitates many metal ions as inner metallic complexes of the first order e.g : [Mg (oxin)₂ ; (10-VII), [Al (oxin)₃] etc. The metal ion is inactivated by a strong complexation and due to its insolubility. is thrown out of solution. If we use 8-hydroxy-quinoline-5-sulphonic acid the metal ions would not be precipitated out of solution but would remain in solution, still in an inactivated form (10-VIII).
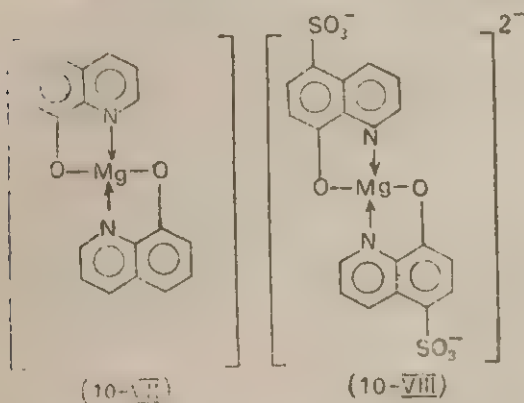
(10-VII)

(10-VIII)

The sulphonic acid derivative thus acts as a sequestering agent Of the many sequestering agents studied ethylenediaminetetraacetic acid anion (EDTA) is very effective. The complexes formed by this polydentate ligand are extremely stable to dissociation and are also quite soluble. Many otherwise non-specific organic precipitation reactions have been rendered highly specific in the presence of EDTA as a masking or sequestering agent. An elaborate account of EDTA as a complexometric titrant appears in section 1.16.2.

10.9. TYPES OF ISOMERISM

Two or more chemical compounds with same empirical composition but with different properties are called isomers. 'Isos' means 'the same' and 'meros' means 'the parts'. Isomers have the same number of same kind of atoms but these are bonded in different manner. The phenomenon that gives rise to isomers is called

isomerism. Isomerism in carbon compounds is restricted mainly to structural isomerism (ortho-, meta- and para-substituted compounds), geometrical isomerism (e.g. maleic and fumaric acids), optical isomerism (*d*- and *l*-tartaric acids) and conformation/rotational isomerism (chair and boat forms of cyclohexane and its derivatives). In the area of coordination complexes isomerism arises out of varied chemical linkages and complexity in stereochemical relationships, and are more diverse than isomerism in organic compounds.

10.9.1. Ionisation Isomerism: Ionisation isomers are produced by an inter-change of position of coordinating ions (ligands) inside the complex zone and anions outside the complex zone. They yield therefore different ions in solution. Examples are:

$$[Co(NH_3)_5Br]SO_4 \quad \text{and} \quad [Co(NH_3)_5SO_4]Br$$
$$[Co(NH_3)_4Cl_2]NO_2 \quad \text{and} \quad [Co(NH_3)_4Cl(NO_2)]Cl$$
$$[Pt(NH_3)_4Cl_2]Br_2 \quad \text{and} \quad [Pt(NH_3)_4Br_2]Cl_2$$
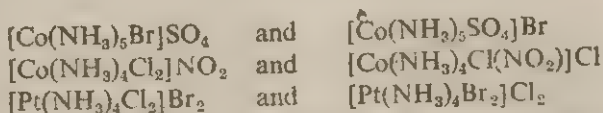
Ionisation isomers are readily detected by quick determination of conductance in solution, and by chemical tests.

Thus bromopentammine cobalt (III) sulphate will react with barium chloride to precipitate immediately barium sulphate but will not immediately precipitate silver bromide with silver nitrate. The conductance will be close to that of a bi-bivalent compound. On the other hand, sulphato pentammine cobalt (III) bromide provides no immediate precipitate of barium sulphate on the addition of barium chloride. Besides, the complex ion will behave as a uni-univalent ion. *Whereas in $[Co(NH_3)_5Br]SO_4$ bromide ion is a ligand, in $[Co(NH_3)_5SO_4]Br$ it is not.*

10.9.2. Hydrate Isomerism : *This isomerism arises out of different disposition of aqua molecules inside and outside the first sphere of attraction.* Unfortunately the examples that have so far appeared in texts are not happy ones and can be considered merely as further examples of ionisation isomers only. The examples cited are those of chromium (III) chloride hydrates. The three hydrates are: (1) violet $[Cr(H_2O)_6]Cl_3$ which does not lose water over conc. H_2SO_4 and the entire chloride is precipitated by silver ion; (2) green $[Cr(H_2O)_5Cl]Cl_2.H_2O$ loses one H_2O over conc. H_2SO_4 and two chloride ions are readily precipitated as AgCl. (3) $[Cr(H_2O)_4Cl_2]Cl.2H_2O$, also green, loses two H_2O over conc. H_2SO_4 and only one chloride gets immediately precipitated by silver nitrate. (1), (2) and (3) behave (on immediate conductance measurements) as tri-uni, bi-uni and uni-univalent electrolytes. Further examples covering both ionisation and hydrate isomerism are:

$$[Cr(en)_2(H_2O)_2]Br_3 \quad \text{and} \quad [Cr(en)_2(H_2O)Br]Br_2.H_2O$$
$$[Co(NH_3)_4(H_2O)Cl]Cl_2 \quad \text{and} \quad [Co(NH_3)_4Cl_2]Cl.H_2O$$
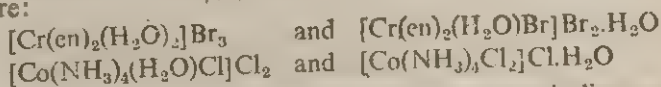
A better example of hydrate isomerism is found in cream and olive green coloured varieties of bis (quinaldinato) oxovanadium (IV):

$[VOQ_2.H_2O]$ $[VOQ]H_2O$ $[QH = $ quinaldinic $=$
olive green   cream   acid   —COOH]
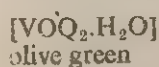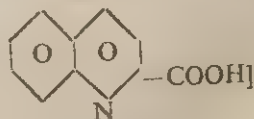
Thermal decomposition curves indicated that the olive-green variety lost the coordinated water around 170—180°C whereas the cream coloured isomer lost the water below 100°C. The cream coloured variety was obtained by the reaction of $VOSO_4$ and QH in water, and the olive green variety in methanol.

10.9.3. Coordination Isomerism : *Such isomeric forms are exhibited when both the cation and the anion of a salt are complexes and there occurs a redistribution of the ligands between the two coordination zones:*

$$[Co[NH_3)_6] [Cr(ox)_3] \quad \text{and} \quad [Cr(NH_3)_6] [Co(ox)_3]$$
$$[Co(NH_3)_6] [Cr(CN)_6] \quad \text{and} \quad [Cr(NH_3)_6] [Co(CN)_6]$$
$$[Cu(NH_3)_4] [PtCl_4] \quad \text{and} \quad [Pt(NH_3)_4] [CuCl_4]$$
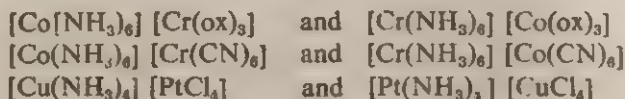
The same metal ion may also function as a central unit in both cation and anion eg: $[Cr(NH_3)_6] [Cr(SCN)_6]$ and $[Cr(NH_3)_4(SCN)_2] [Cr(NH_3)_2(SCN)_4]$.

10.9.4. Ligand Isomerism: *If two ligands are isomeric to each other their complexes with similar composition necessarily become isomeric.* Thus trimethylene-diamine (tn) and propylenediamine (pn) form isomeric complexes, $[Co(pn)_2Cl_2]Cl$ and $[Co(tn)_2Cl_2]Cl$. Picolinic acid (pyridine α-carboxylic acid, PicH) and nicotinic acid (pyridine β-carboxylic acid, NicH) form, for example, isomeric inner metallic complexes with bivalent silver $[Ag(Pic)_2]$ and $[Ag(Nic)_2]$.

10.9.5. Linkage Isomerism : Some coordinating groups possess two different donor atoms. *Linkage isomerism arises out of two modes of attachment of the ligand to the central metal ion through two different donor atoms.* Thus NO_2^- group may link via nitrogen (nitroisomer) or via oxygen (nitrito), e.g: yellow brown nitropentammine cobalt (III) chloride $[Co(NH_3)_5(NO_2)]Cl_2$ and the red nitrito pentammine cobalt (III) chloride $[Co(NH_3)_5(ONO)]Cl_2$. Two isomeric forms involving the thiocyanate ion are also known: $[Pd(dipy)(SCN)_2]$ and $[Pd(dipy)(NCS)_2]$.

$$K_2[Pd(SCN)_4] + dipy \xrightarrow{-78°C} [Pd(dipy)(SCN)_2] + 2KSCN$$

orange yellow

| solid heated to 150°C

$$K_2[Pd(SCN)_4] + dipy \xrightarrow{25°C} [Pd(dipy)(NCS)_2] + 2KSCN$$

light yellow
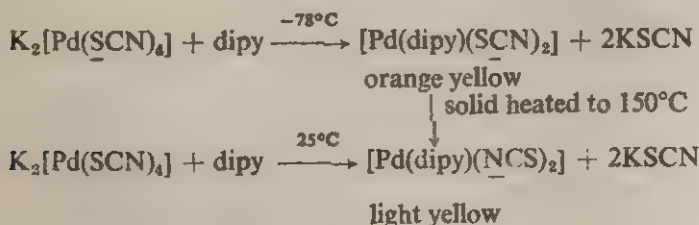
Besides NO_2^- and SCN^- groups there are other ligands which are capable of playing double role, such as CN^-; $S_2O_3^{2-}$, $(NH_2)_2CO$, $(CH_3)_2SO$. However, actual isomeric compounds have not yet been fully established with any of these ligands. Thiosulphatopentammine cobalt (III) salts obtained by Rây as purple crystals by air oxidation of cobalt (II) salts, thiosulphate and ammonia is now

believed to be a mixture of 90% $[H_3N)_5CO-O-S_2O_2]^+$ and 10% $[(H_2N)_5Co-S-SO_3]^+$ as evidenced from infrared studies (also see section 19.5.3).

The less stable of a pair of linkage isomers often reverts to the more stable form. The less stable form is likely to exist at low temperature and with those metal ions which are known to form kinetically inert complexes (Co^{3+}, Pt^{2+}, Pd^{2+}).

The above mentioned ligands with two possible sites for attachment to the metal ion are called ambident (or ambidentate) ligands.

It may be mentioned that the older naming of this isomerism as salt isomerism has now been replaced by the appropriate linkage isomerism.

10.9.6. Stereoisomerism: *This is a form of isomerism in which two complexes of identical first sphere composition differ in the relative positions of the coordinating groups. Such isomers are also termed geometrical isomers, for these isomers give rise to different arrangements of coordinating groups within the same overall geometry of the complex zone.* Some (not all) of the geometrical isomers may develop optical activity due to distinct mirror image forms. Thus optical isomers may be isolated from a particular geometrical isomer which is capable of existing in non-superimposable mirror-image forms.

Geometrical Isomerism: Of the three important and rather common stereo-chemistries (tetrahedral, planar and octahedral) geometrical isomerism cannot arise in a tetrahedral structure, because in a tetrahedron each ligand is equidistant from the other three and all bond angles are the same (109°). But in square planar and octahedral complexes abundant examples are known.

In square planar MA_2B_2 type complexes the following geometrical isomers are observed: a *cis*-planar structure obtains when the two A groups or the two B groups occupy near neighbour positions, and a *trans*-planar geometry when they

cis-planar

Superimposable mirror image;
no optical activity,

trans-planar

mirror image superimposable after
rotation; no optical activity
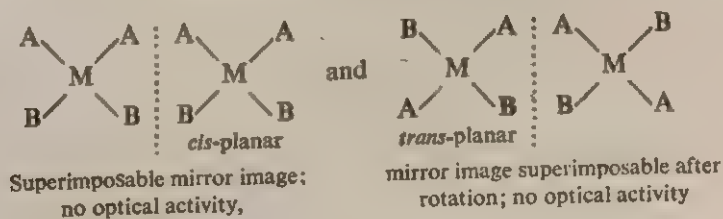
occupy the distant most positions. $[Pt(NH_3)_2Cl_2]$ exists in two isomeric forms. Complexes of the type MA_2BC can also exist in two geometrical isomers. It is not possible to obtain optical isomers of a square planar complex with monodentate ligands, whatever the composition is: MA_2B_2; MA_3B. However optical activity may be induced in square planar geometry with two monodentate ligands and one bidentate ligand having an asymmetric centre. In a very special case optical activity has been developed as a result of coordination. Thus in the complex dinitro(N-methyl N-ethyl glycinato) platinate (II), the ammine nitrogen is rendered asymmetric through coordination to the metal ion. The nitrogen is linked to four different groups: the methyl, the ethyl, the $-CH_2$ group and the platinum (II).

In octahedral stereochemistry interesting cases of geometrical isomerism occur. When one of the A groups of $[MA_6]$ is replaced by a B group giving $[MA_5B]$ no geometrical isomerism can occur. This is because whichever position of the octahedron is occupied by B it will be at 90° from four M—A groups and at 180° from the fifth M—A group. When a further replacement is made leading to $[MA_4B_2]$ there occur two geometrical isomers, one cis and the other *trans* eg: $[Co(NH_3)_4Cl_2]Cl$. (10-1X and 10-X)
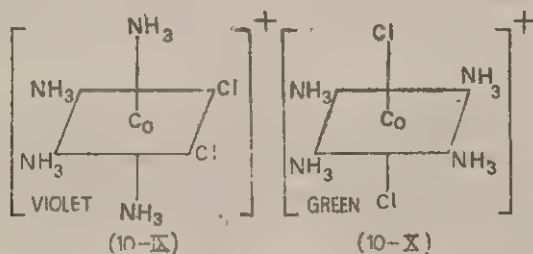
Cis-dichloro tetrammine   Trans-dichloro tetrammine
cobalt (III) (Violet)   cobalt (III) (Green)

A very large number of complexes of this type are known eg: cis$[Co(NH_3)_4(NO_2)_2]$ X (yellow-brown) and *trans* $[Co(NH_3)_4(NO_2)_2]$ X (yellow); cis $[Co(en)_2Cl_2]Cl$ (purple) and *trans* $[Co(en_2Cl_2]Cl$ (green); cis $[Cr(en)_2(NCS)_2]NCS$ (orange red) and *trans* $[Cr(en)_2(NCS)_2]NCS$ (yellow orange). Complexes of the type $[MA_3B_3]$ ($[Co(NH_3)_3(NO_2)_3]$, $[Co(NH_2—CH_2—COO)_3)]$ are also capable of exhibiting two geometrical isomers, although the structures of such isomers have not yet been fully established.

Determination of configuration of geometrical isomers: With the present state of knowledge about complexes, there are in fact several techniques by which configuration of geometrical isomers can be determined. The simplest technique is to study the action of bidentate chelating ligands on the geometrical isomers, where isomerism is due to different disposition of two monodentate groups. Bidentate ligands are capable of enforcing a 5-membered or a 6-membered ring at the metal ions, and with this ring size it is possible only to span two nearest positions around the metal ion. Examination of models shows that usual bidentate chelating ligands cannot span the furthest points, that is, *trans* psotions. Hence suitable substitution reactions by chelating ligands on geometrical isomers with monodentate groups will throw some light on the cis-trans configuration of the complex. Provided that no change in configuration takes place during substitution reactions, that isomer which reacts with a chelating ligand or which is formed by the displacement of a chelating ligand must belong to the cis series. Such reactions have often been tried for geometrical isomers in both octahedral and square planar stereochemistry. A typical example is given in Chart 10-II below. The determination of the cis configuration involves the reaction of a binuclear complex with concentrated hydrochloric acid to give one mole of the dichloro complex and one mole of the diaquo complex. Provided that no change in configuration has occurred

during the displacement of the chelating carbonato group or the μ-dihydroxo compound, the two chloro groups and the two aquo groups must be occupying adjacent positions and hence must be *cis* complexes. Note also that treatment of the carbonato complex with HCl instead of with H_2SO_4 leads to a change in configuration.

$$\text{dil HCl}$$
$$\text{[Co(NH}_3\text{)}_4\text{CO}_3\text{]}^+ \xrightarrow{\hspace{2cm}} \text{[Co(NH}_3\text{)}_4\text{(H}_2\text{O)Cl]}^{2+}$$

dil. $\downarrow$ H_2SO_4 conc. $\downarrow$ H_2SO_4 : HCl

$[Co(NH_3)_4(H_2O)_2]^{3+}$ $[Co(NH_3)_4Cl_2]^+$

aq. $\downarrow$ NH_4OH green

$[Co(NH_3)_4(H_2O)(OH)]^{2+}$ *TRANS* Series

heat $\downarrow$ 100°C

$$[NH_3)_4Co\underset{OH}{\overset{OH}{\diagup\diagdown}}Co(NH_3)_4]^{4+}$$

conc. $\downarrow$ HCl (-12°C)

$\longrightarrow [Co(NH_4)_4Cl_2]^+ + [Co(NH_3)_4(H_2O)_2]^{3+}$

     Purple   Purple

CIS Series

(left margin: HCl (alcohol))
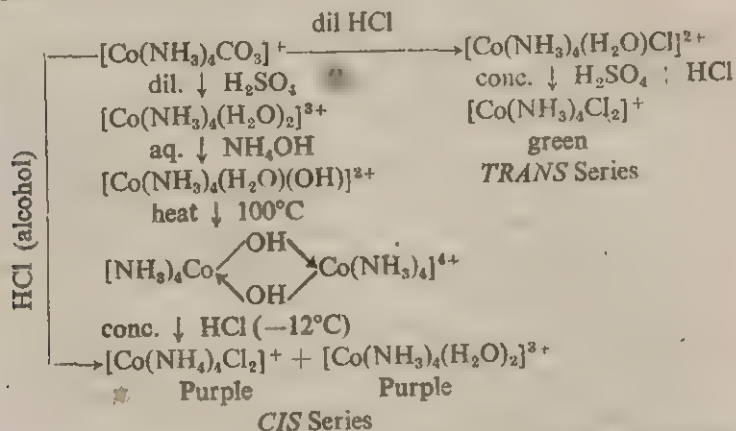
Chart 10-II. Substitution reactions elucidating configurations of geometrical isomers.

Certain other methods may just be hinted at. A *cis* complex has a higher dipole moment than the symmetrical *trans* complex. A *cis* complex has a higher molar extinction coefficient (absorption) than the corresponding *trans* complex and sometimes the two isomers may differ significantly in their absorption spectra. *Cis* and *trans* derivatives have sometimes been characterised through different vibrational properties of the attached coordinating groups. A common obligatory technique, however, is to attempt to resolve the *cis* complex into the two possible optically active isomers.

Determination of cis-trans configuration of platinum (II) complexes: Based on the assumption that a four membered or a five membered chelating ligand can only span *cis* positions substitution reactions by bidentate oxalate or glycine ligand on monodentate ligands gives a mono (oxalato) or a mono (glycinato) complex in the case of a *cis*-complex while for the *trans*-complex two glycinate or two oxalate ions are found inside the coordination sphere functioning as a monodentate ligand:

$$\begin{array}{c}H_3N\\H_3N\end{array}\!\!\!\underset{}{\diagdown}Pt\underset{Cl}{\overset{Cl}{\diagup}} + H_2NCH_2COOH \longrightarrow \left[\begin{array}{c}H_3N\\H_3N\end{array}\!\!\!\diagdown Pt\diagup\begin{array}{c}O-C=O\\ |\\NH_2-CH_2\end{array}\right]Cl$$

cis

$$\begin{array}{c}H_3N\\Cl\end{array}\!\!\!\diagdown Pt\diagup\begin{array}{c}Cl\\NH_3\end{array} + 2H_2NCH_2COOH \longrightarrow$$

trans

$$\left[\begin{array}{c}H_3N\\HOOC.CH_2NH_2\end{array}\!\!\!\diagdown Pt\diagup\begin{array}{c}NH_2.CH_2.COOH\\NH_3\end{array}\right]Cl_2$$
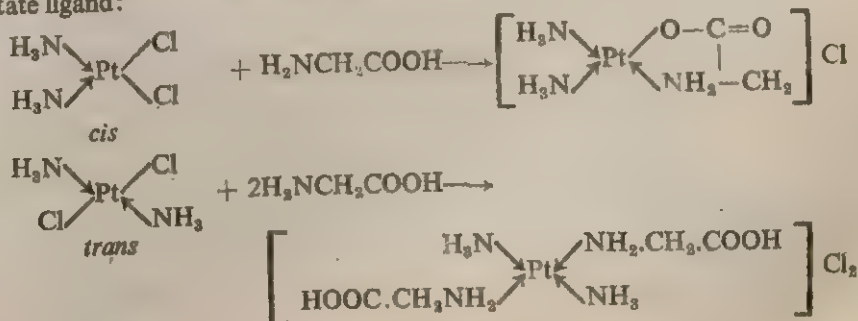
Kurnakov observed that the above *cis* and *trans* varieties react with thiourea (tu) to give $[Pt(tu)_4]Cl_2$ and *trans* $[Pt(tu)_2(NH_3)_2]Cl_2$ respectively. In the case of the *cis* complex first the two thiourea ligands substitute the two *cis* chlorine and then they labilise the two *trans* positions because of their very high *trans* labilising effect resulting in total substitution of the coordinated groups. Such total substitution is not possible with the *trans* derivative. Dipole moment measurements have also helped in establishing the *cis-trans* (square planar) geometry of the two forms of $[(R_3P)_2PtCl_2]$ and $[(R_3As)_2PtCl_2]$. One of the forms showed zero dipole moment while the other had about 10 Debye. The zero dipole moment is possible if each pair of Pt—Cl, Pt—P or Pt—As is collinear- which again is possible if the complex has *trans* planar configuration. The tertiary phosphine and the tertiary arsine groups were chosen because these have one lone pair and hence the resultant moment will be along the direction of the coordinate link. Finally X-ray crystal structures have unequivocally established the planar geometry in both *cis* and *trans* $[Pt(NH_3)_2Cl_2]$.

Optical Isomerism: When two isomers are so related that the arrangement of donor groups around the central atom in one is the mirror image of the other and further that one is not superimposable on the other, then the isomers develop optical activity, and are known as optical isomers. Optical isomers are related in the same way as the left hand is to the right. An optically active substance can rotate the plane of polarised light transmitted through it. When the plane of the light is rotated to the right the substance is called dextrorotatory (*d* form) and when rotated to the left it is levorotatory (*l* form). On the contrary, if the polarised light remains unaffected, the compound is inactive or racemic. A racemic substance is composed of 50% *d*-and 50% *l*-form.

INACTIVE TRANS   OPTICALLY ACTIVE CIS ISOMERS (d and l)
(10-XI)   (10-XII)
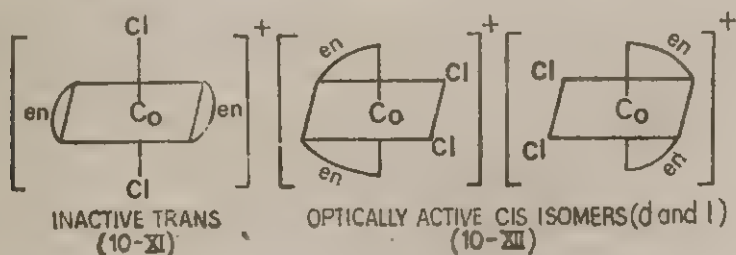
Optical isomers arise in complexes of the type $[M(AA)_2B_2]$ due to the existence of geometrical isomers. The *cis* variety can exist in two distinct mirror image forms which are not superimposable (not obtainable by mere rotation of one form). On the contrary, the *trans* form being symmetrical provides only superimposable mirror images, that is, only one distinct form (cf. 10-XI and 10-XII). Optical isomers occur also with tris (bidentate chelate) complexes eg: in $[Co(en)_3]^{3+}$ (10-XIII), $[Co(ox)_3]^{3-}$, $[Co(BigH)_3]^{3+}$, $[Ni(dipy)_3]^{2+}$ etc. In the given structures 'en' stands for the bidentate neutral ligand ethylenediamine.

Under normal conditions of synthesis, a potentially optically active complex consists of a racemic mixture i.e. equal amounts of dextro- and levorotatory forms.

OPTICAL ISOMERS OF $\{Co(en)_3\}^{3+}$
(10-XIII)
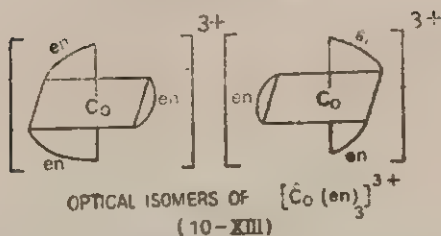
The commonest method of separating of racemic complex into the d- and l-isomers involves preparing salts of the complex ion with optically active cations or anions, thus forming diastereoisomeric salts:

$$\left\{ \begin{array}{c} d\text{M} \\ + \\ l\text{M} \end{array} \right. + l\text{A} \longrightarrow \underbrace{d\text{M } l\text{A} + l\text{M } l\text{A}}_{\text{pair of diastereoisomers}}$$
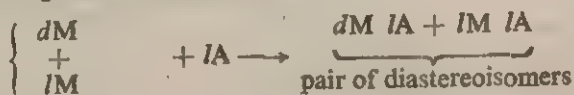
Diastereoisomerism occurs due to the presence of two sources of dissymmetry in a molecule. Diastereoisomers are usually optically active but are not mirror images of each other. They are a pair containing two optically active centres of which one is common to both while the other two are non-superimposable mirror images of each other. dM and lM are the dextrorotatory and levorotatory forms of the optically active cation M. lA is an optically active anion. Their combination gives a pair of salts, which do not have the same optically active partners in their cations and anions. Hence the diastereoisomeric salts differ appreciably in their physical properties, particularly in solubility because of the differences in interaction between the cation and the anion. Fractional crystallisation, commonly from aqueous medium, leads to a separation of the two diastereoisomers. The pure diastereoisomers are separately treated with suitable non-optically active salts to recover the d- and l- forms of the complex as salts of non-optically active cations or anions, that is, as enantiomers. Enantiomers are stereoisomers with non-superimposable mirror images.

$$d\text{M} \quad l\text{A} \quad \xrightarrow{\text{KI}} \quad d\text{M I} + \text{K}l\text{A}$$

$$l\text{M} \quad l\text{A} \quad \xrightarrow{\text{KI}} \quad l\text{M I} + \text{K}l\text{A}$$
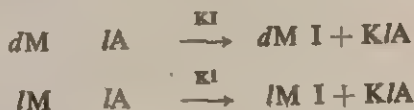
Thus $[Co(en)_3]^{3+}$ when reacted with d-tartrate ion provides the two diastereoisomeric salts, d-$[Co(en)_3]Cl. d$-tart and l-$[Co(en)_3]Cl. d$-tart. Fractional crystallisation leads to the separation of d-$[Co(en)_3]Cl. d$-tart as the less soluble fraction and the l-$[Co(en)_3]Cl. d$-tart as the more soluble one. Treatment of the two salts with excess ammonium sulphate results in the isolation of pure d-$[Co(en)_3]$ $(SO_4)_{1.5}$ and l-$[Co(en)_3](SO_4)_{1.5}$. Treatment with barium chloride gives the chloride salts of the optically active cations. *The technique of separation of a racemic substance into the two optically active enantiomers is called reslution.* Resolution of anionic complexes is carried out via formation of diastereoisomeric salts with optically active bases like strychnine and cinchonine. Once again it is expected that l-strychnine or l-cinchonine salts of the optically active complex anion will

differ in their solubilities. Thus a separation of the two diastereoisomers is possible. The separated diastereoisomers are then treated with some suitable salts (say KI) when the potassium salts of the dextro and the levo forms of the optically active enantiomers will be obtained.

Other less common and less used methods include induced crystallisation. Thus Werner seeded a solution of recemic $[Co(en)_2(C_2O_4)]^+$ with a few crystals of d-$[Co(en)_2(C_2O_4)]^+$ when the *dextro isomer* started crystallising. Besides, electrophoresis sometimes helps in the segregation of one of the two ionic enantiomers towards one of the two electrodes. It is interesting to note that optically active complex cations and anions themselves have also been used as resolving agents. Thus d $[Co(en)_3]^{3+}$ has been utilised in resolving K[Co(EDTA)]. It is obvious that resolution of non-electrolytic complexes such as $[Co(gly)_3]$ cannot be effected via diastereoisomeric method. Glycinate ligand is $NH_2-CH_2-COO^-$. It is thus a bidentate NO donor. The structure of tris (glycinato) cobalt (III) admits of two varieties: (a) *cis:* where the three N atoms as also the three O atoms are relatively *cis* (b) *trans:* where two of the three N atoms as also two of the three O atoms are relatively *trans*. Since the complex is a tris (bidentate) type both the *cis* and the *trans* forms are resolvable. Resolution of such complexes is effected by adsorption of the isomers to different degrees on cellulose, lactose or starch column followed by elution with suitable eluting agents. *Resolution is only possible when the isomers are kinetically stable and do not rearrange rapidly.*

Stereoisomerism in Tetrahedral Complexes: Examination of models shows that a tetrahedral metal complex, as is true of tetrahedral carbon, can exhibit stereoisomerism only when all the groups attached to the metal ion are different eg: in [Mabcd]. Such a complex can exist in two optically active isomeric forms although none has been prepared yet. Where stereoisomerism is possible in tetrahedral complexes it must be in the form of optical isomerism and not as geometrical isomerism. Note that the two mirror images of Mabcd cannot be obtained by mere rotation of one form or the other around some suitable element of symmetry. (Fig. 10.2a). The reader should also convince himself that for [Ma₂bc] type complexes the mirror images are obtainable by suitable rotations and hence such mirror images are superimposable and do not possess distinct identity:

(a)   (b)
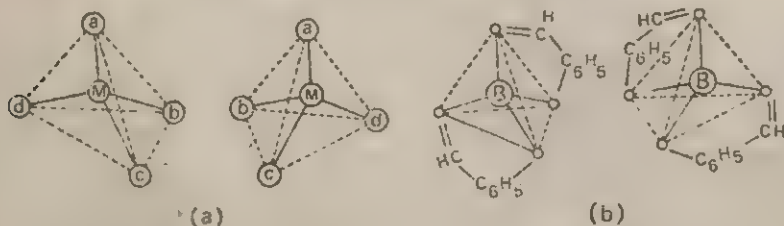
F,G. 10.2. Optical isomers in tetrahedral complexes

Asymmetry and consequently optical activity may be introduced in tetrahedral structures by sufficiently unsymmetrical chelating ligands. Bis (salicy-

ladehydato) boron (III) (Fig. 10.2b), and bis (benzolypyruvato) beryllium (II) have been resolved into optical isomers, thus proving that the complexes possess tetrahedral rather than square planar structure. Latter stereochemistry would not admit of distinct, non-superimposable mirror images.

10.9.7. Conformation (Polytopal) Isomerism: Unique pairs of conformation isomers have been isolated for certain nickel (II) complexes eg: the green and brown forms of $[Ni(PEtPh_2)_2Br_2]$ which are interconvertible. The green form is tetrahedral while the brown form is planar. Since these isomers differ only in the L-M-L angle, the name *allogons* ('allos' meaning 'different' and 'gonia' meaning

DARK GREEN, PARAMAGNETIC
(10-XIV)

DARK BROWN, DIAMAGNETIC
(10-XV)
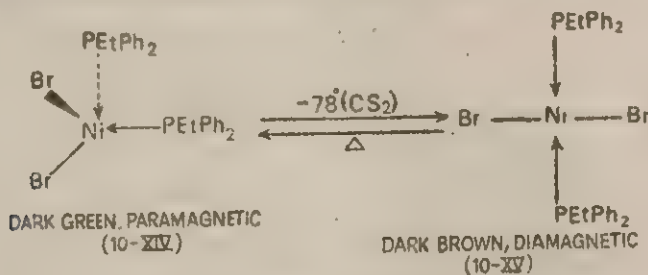
'angle') has been proposed for such isomers. Conformation isomers have the same coordination number but different stereochemistries. Interconversion of two isomers via an intramolecular pathway needs some flattening motion of the tetrahedron to arrive at the square planar geometry as shown below (Fig. 10.3):

Tetrahedral   Square planar
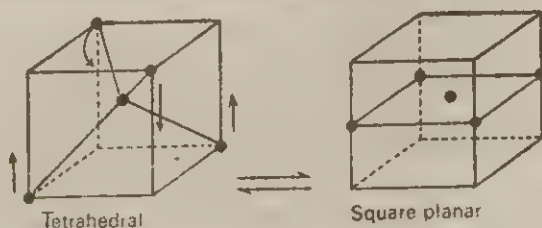
Fig. 10.3. Flattening motion of a tetrahedron

10.9.8. Spin State Isomerism: Crystal field theory predicts that for d^4, d^5, d^6 and d^7 ions alone in octahedral geometry there may arise spin state equilibrium between isomeric high-spin and low-spin octahedral forms provided the ligand has a crystal field strength close to the respective cross-over region (see section 10.11.2 and Fig. 10.8). For d^8 nickel (II), however, maximum cases of spin state isomerism have been identified. In these cases the different spin states, arise due to varying degree of tetragonal distortion (near octahedral and near square planar) in a mixed ligand complex of the type Nia_4b_2(e.g. $a =$ NN'diethylthiourea and $b =$ Cl$^-$) or Ni(N—N—N—N)X$_2$.H$_2$O (N—N—N—N being a macrocyclic ligand with four nitrogen donors in the equatorial plane and X being Cl$^-$ or Br$^-$). Magnetic moments in such cases lie somewhere in between the high-spin octahedral ($\mu = 3.0$ 3.3 B.M) value and the low-spin square planar value ($\mu = 0$). Tempera-

ture variation will shift the equilibrium this way or that way depending on which spin form makes up the ground state. The conformation isomer cited in 10.9.7 may also be considered as an example of spin state isomers.

10.10. VERFICATION OF OCTAHEDRAL STEREOCHEMISTRY

A very extensive study of the geometrical and optical isomers of complexes with coordination number six revealed that octahedral geometry is the preferred stereochemistry. In order to dispel the claim of two other geometries capable of admitting six groups, namely a hexagon and a trigonal prism, Werner worked out the number of geometrical isomers that each of these geometries admitted for a particular complex and then compared with the number of experimentally isolated isomers. A single form is predicted by each model for complexes $[MA_6]$ and $[MA_5B]$. But for complexes $[MA_4B_2]$ both the hexagon and the trigonal prism predict three isomers, namely (1, 2), (1, 3) and (1, 4) but the octahedron predicts only two (1, 2) and (1, 6) (Fig. 10.4). Experimentally no more than two geometrical isomers have been isolated for metal complexes of the type $[MA_4B_2]$. Similarly for $[MA_3B_3]$ complexes the octahedral model predicts two geometric isomers and experiments corroborate this number.
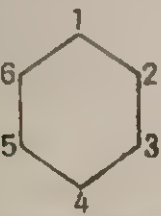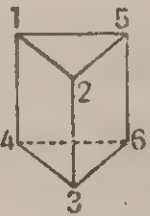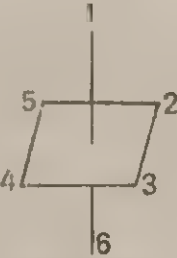
	PLANE HEXAGONAL	TRIGONAL PRISMATIC	OCTAHEDRAL
MA_5B	ONE	ONE	ONE
MA_4B_2	THREE (1,2; 1,3; 1,4)	THREE (1,2; 1,3; 1,4)	TWO (1,2; 1,6)
MA_3B_3	THREE (1,2,3; 1,2,4; 1,3,5)	THREE (1,2,3; 1,2,5; 1,2,6)	TWO (1,2,3; 1,2,6)

FIG. 10.4. Possible geometrical isomers with three models.

Furthermore the octahedral model alone correctly predicted the optical activity in complexes. For example the hexagon and the trigonal prism would predict no optical isomers of a complex $[M(AA)_3]$ (AA = bidentate ligand) but the octahedron requires the existence of two distinct mirror-image forms. A large number of complexes of this type have actually been resolved into optically active enantiomers. Werner therefore concluded that the preferred geometry of six-coordinate complexes is the octahedron. The octahedral stereochemistry has since been

confirmed by crystal structure determination of numerous six-coordinate complexes.

To prove that the optical activity in coordination complexes did not arise out of the carbon atoms present in the organic ligands, Werner successfully synthesised a purely inorganic complex $[Co(AA)_3]^{6+}$, $\left(\text{where AA is } (NH_3)_4Co\diagdown\begin{array}{c}OH\\OH\end{array}\right)^+$ and resolved this complex into two optical isomers. The complex was obtained by the action of ammonia on the chloroaquotetrammine cobalt (III) salts. A

(10-XVI)   (10-XVII)
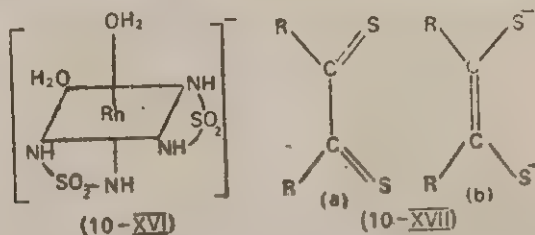
second purely inorganic optically active complex was synthesised by Mann by reacting a rhodium (III) salt with sulphamide $SO_2(NH_2)_2$. The complex isolated as a sodium salt has the formula $Na[Rh(NH-SO_2-NH)_2(H_2O)_2]$. The sulphamide anion in the complex functions as a dibasic, bidentate ligand. The complex was resolved into optical isomers indicating the *cis structure* (10-XVI).

Recently trigonal prismatic coordination has been established in metal tris (dithienes) $[M(S_2C_2R_2)_3]$ (M = V, Cr, Mo, W, Re). These compounds are rather unorthodox and the ligands have neither the structures of neutral dithiodiketones (10-XVIIa) nor of dithiolato dianions (10-XVIIb). Orthodox definition of metal

(10-XVIII)

oxidation state cannot be offered for such complexes. However structural determinations have been made and the idealised structure of a trigonal prismatic dithiene complex (10-XVIII) has been established.
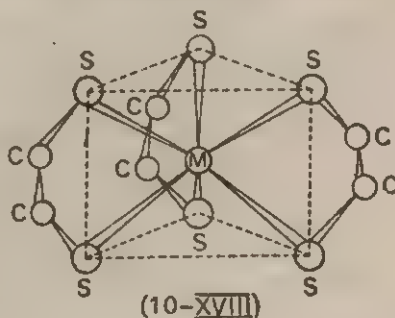
10.11. THE NATURE OF THE COORDINATE LINKAGE

There are three major approaches to the study of the nature of the coordinate linkage: (1) Valence Bond Theory (2) Crystal Field Theory (3) Molecular Orbital Theory. Of these valence bond (VB) theory propounded by Pauling is the oldest and is based on the conception of hybridisation of suitable orbitals of the metal ion. The VB theory has served inorganic chemists very well during two decades 1930-1950 and had provided a useful understanding of the valence and structure of coordination complexes. After 1950 the quantitative inadequacy of the theory

was gradually realised and crystal field theory gained ground. Crystal field theory assumes the ligands as dipoles or ions and examine the effect that these dipoles or ions force on the ordering of the d-orbitals of the transition metal ions. Molecular orbital (MO) theory largely considers that there is a good overlap of the orbitals of the ligands and the metal ions so that the bonding turns out to be largely covalent. Below we present a discussion on the first two theories:

10.11.1. Valence Bond Theory: The formation of a complex between a given metal ion and certain ligands is assumed to follow the course enunciated below:

(a) The metal M first loses requisite number of electrons to form the ion, the number of electrons thus lost being the valence of the resulting cation.

(b) The metal ion will make available a number of orbitals, equal to its coordination number, for the formation of covalent bonds with the ligands. Since metal complexes attain certain definite stereochemistry, metal ion orbitals must be so disposed that they point to such stereochemical directions. Metal ion orbitals (s, p or d) cannot generate on their own such stereochemistries as tetrahedral, octahedral, square pyramidal and so on. Pauling therefore invoked the hybridisation of suitable pure metal ion orbitals so that the desired stereochemistry is attained. The types of hybridisation occurring in the first row transition metal compounds are the following:

$4s\,4p^3\,(sp^3)$	: 4 coordinate, tetrahedral
$3d_{x^2-y^2}\,4s\,4p^2\,x/y(dsp^2)$	: 4 coordinate, square planar
$3d_z\,4s\,4p^3\,(dsp^3)$	: 5 coordinate, trigonal bipyramidal
$3d^2_{z^2}/_{x^2-y^2}\,4s4p^2(d^2sp^2)$	: 5 coordinate, square pyramidal
$4s\,4p^34d^2_{z^2}/_{x^2-y^2}(sp^3d^2)$	: 6 coordinate, octahedral (*outer orbital*)
$3d^2_{z^2}/_{x^2-y^2}\,4s4p^3(d^2sp^3)$	: 6 coordinate, octahedral (*inner orbital*)

(c) The hybridised orbitals are so directed as to facilitate their occupation by electron pairs coming from the donor ligands. Effectively there occurs an overlap of a filled ligand orbital and an empty hybrid orbital of the metal ion. (M←L).

(d) The non-bonding electrons of the metal ion are then reorganised to occupy the remaining metal orbitals (pure d, s or p as the case may be). The regrouping of electrons is achieved obeying Hund's rule, that is, with maximum possible unpaired spins.

(e) In addition to the σ-bond a π-bond may be formed by overlap of a filled, suitable metal d-orbital with a vacant ligand orbital: M ⇌ L. Such double bonding usually occurs in complexes of metal ions in low oxidation states.

A given stereochemistry involves a particular hybridisation utilising certain d-orbitals. The orbitals available for non-bonding electrons are therefore the dictates of the stereochemistry. Again the number of d-orbital electrons remaining

indicates the valence of the central ion. These points are illustrated in Chart 10-III below with respect to iron (III).

Chart 10-III. Valence Bond Theory as applied to iron (III). (↑ or ↓) represents the spin of a non-bonding electron, X denotes a bonding ligand electron and n, number of unpaired electrons.

Electrons in an incompletely filled shell give rise to a resultant spin angular momentum. The orbital moment is considered largely quenched by the surrounding ligands. Thus ignoring orbital contributions, the magnetic moment of a complex will depend on the actual number of unpaired electrons (Table 10.3).

Table 10.3. Magnetic Moments of Complexes of First Transition Series

Configuration	Example	Stereochemistry	Hybridisation	Unpaired electrons	μ(B.M.) spin only	Exptl.
d^1	$K_3[TiF_6]$	Octahedral	d^2sp^3	1	1.73	1.70
	$[VO(acac)_2]$	Square pyramidal	d^2sp^2	1	1.73	1.70
d^2	$NH_4V(SO_4)_2$ $12H_2O$	Octahedral	d^2sp^3	2	2.83	2.80
d^3	$[Cr(NH_3)_6]Br_3$	Octahedral	d^2sp^3	3	3.88	3.77
d^4	$[Cr(H_2O)_6]SO_4$	Octahedral	sp^3d^2	4	4.90	4.80
d^5	$Na_3[FeF_6]$	Octahedral	sp^3d^2	5	5.92	5.85
	$K_3[Fe(CN)_6]$	Octahedral	d^2sp^3	1	1.73	2.25
d^6	$[Co(NH_3)_6]Cl_3$	Octahedral	d^2sp^3	0	0	0
	$[Et_4N]_2[FeCl_4]$	Tetrahedral	sp^3	4	4.90	5.40
d^7	$Cs_3[CoCl_4]$	Tetrahedral	sp^3	3	3.88	4.60
	$K_2Ba[Co(NO_2)_6]$	Octahedral	d^2sp^3	1	1.73	1.88
d^8	$[Ni[NH_3)_6]Cl_2$	Octahedral	sp^3d^2	2	2.83	3.32
	$[Ni(BigH)_2]Cl_2$	Square planar	dsp^2	0	0	0
d^9	$[Cu(BigH)_2]Cl_2$	Square planar	dsp^2	1	1.73	1.79

In practice the magnetic susceptibility of a complex is determined whence the magnetic moment and the number of unpaired electrons are deduced (Chapter 11). The number of unpaired electrons is then checked with the number of unpaired electrons permitted by the different stereochemistries. Table 10.4 shows that although the correspondence between the number of unpaired electrons and the stereochemistry, bond type and valence is not always unambiguous, a knowledge of the magnetic moment alongwith other chemical evidences may turn out to be of great practical value in understanding the nature of the complex.

Table 10.4. Values of n (Unpaired Electrons) for different Stereochemistries and Configurations

Number of d electrons	1	2	3	4	5	6	7	8	9
Octahedral, outer orbital sp^3d^2	1	2	3	4	5	4	3	2	1
Octahedral, inner orbital d^2sp^3	1	2	3	2	1	0	1	0	1
Tetrahedral, sp^3	1	2	3	4	5	4	3	2	1
Square planar dsp^2	1	2	3	4	3	2	1	0	1

Deficiencies of Valence Bond Theory :

1. For outer orbital octahedral sp^3d^2 and tetrahedral sp^3 the same number of unpaired electrons are indicated, so that magnetic moment would not distinguish between the two stereochemistries.

2. For d^7, d^8 and d^9 configurations inner orbital octahedral complexes require promotion of non-bonding electrons to some higher orbitals (presumably to $5s$). Such promotions would make the electrons vulnerable to oxidation. This mechanism can explain the easy oxidation of cobalt (II) complexes to cobalt (III) complexes but the same token would predict copper (III) complexes to be as much abundant as those of cobalt (III). Experiments show that copper (III) complexes are hard to synthesise and are very scarce.

3. Although most of the first transition series complexes respond to spin only values for their magnetic moments, certain other ions, for example, nickel (II) and cobalt (II) in tetrahedral and octahedral geometries provide magnetic moments substantially higher than the spin only values (Table 10.3). The enhanced values are not explained by the VB theory.

4. It is now firmly established that both the colour and the magnetic moments of transition metal complexes are due to their possessing d-orbital electrons. Therefore there must be a quantitative connection between spectra and magnetic moment. Unfortunately this connection is not revealed by the VB theory.

10.11.2. Crystal Field Theory : A metal ion in a complex is surrounded by coordinating ligand anions or negative ends of dipolar molecules. An electric field is produced at the metal ion by the surrounding ligand anions or the dipolar

molecules. Such electrostatic field will exert some effect on the electrons of the metal ion. This electrostatic approach towards the interaction between a metal ion and the ligands is known as crystal field theory because it was originally discussed for ions in a crystal lattice (effect of chloride ions on K^+ in KCl lattice). *It is important to record that the crystal field theory considers the ligand atoms as point charges or point dipoles, and does not consider any overlap between ligand orbitals and metal ion orbitals.* Crystal field theory examines the energetics of the d-orbitals, in particular, in given geometries.

Placement of the donor atoms at different stereochemical positions will perturb the d-orbitals of the metal ions to different extent. Several stereochemistries are now chosen for discussion.

Octahedral Complexes: We recall that there exists only one s orbital (with a given n) which is spherically symmetrical. Therefore on applying a field of six negative charges located at octahedral points the energy of the s orbital will be raised compared to the field free situation. The three p orbitals have their lobes concentrated on either side of the nucleus along x (p_x), y(p_y) and z(p_z) axes. Each of these p orbitals faces directly two ligands along the coordinate axes and since all the three p orbitals are also themselves degenerate, all p orbitals will be raised in their energy but there will be no separation (splitting) among the p

Fig. 10.5. The three p orbitals in an octahedral surrounding of six ligands

orbitals themselves (Fig. 10.5). It is important to note that instead of an octahedron if we take a square plane the p_x and p_y orbitals will face the four ligands but the p_z orbital will face none. Hence in a square planar environment there will occur a splitting of p orbitals into two sets, higher one having p_x and p_y and the lower one having the p_z orbital.

The five d-orbitals are degenerate in a field-free ion. The five d-orbitals are not all alike. The three orbitals d_{xy}, d_{xz}, d_{yz} have their four lobes concentrated in between the coordinate axes: for example d_{xy} orbital has its four lobes between the x and y axes. The $d_{x^2-y^2}$ orbital has its lobes along the x and the y axes. The d_{z^2} orbital has two lobes along the z-axis and a concentric lobe all around the nucleus in the xy plane. When such a set of five d-orbitals is subjected to an octahedral crystal field the d-orbitals can no longer remain degenerate. Their overall energy is raised from that in the absence of any field, and they undergo splitting. Since the $d_{x^2-y^2}$ and the d_{z^2} orbitals are face to face with the six ligands they are now raised in energy whereas the d_{xy}, d_{xz}, d_{yz} orbitals are lowered in energy. The splitting is so adjusted that the centre of gravity (baricentre) of the five degenerate d-orbitals in a uniformly smeared out field of six negative charges is maintained (Fig. 10.6). The difference in energy of the orbitals d_{xy}, d_{xz}, d_{yz} (t_{2g} set) and the $d_{x^2-y^2}$, d_{z^2} orbitals (e_g set) is given as symbol $\triangle$ or 10 Dq, this difference being a measure of the strength of the crystal field operating on the metal ion. $\triangle$ or 10 Dq is the separation between the t_{2g} (d_{xy}) and the e_g ($d_{x^2-y^2}$) and is known as the *crystal field splitting parameter* or as the *crystal field strength*.

Since the pre-splitting centre of gravity is to be maintained the e_g set will go up by say x and the t_{2g} set will go down by say y. If E is the energy of each electron prior to splitting it follows that:
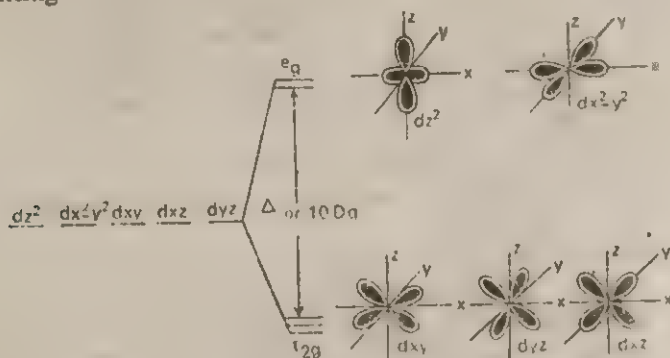
FIG. 10.6. Splitting of the d-orbitals in an octahedral field.

$$10E = 4(E + x) + 6(E - y) \text{ so that } 2x = 3y.$$

Also since $x + y = \triangle$ we have $x = \frac{3}{5} \triangle = 6 Dq$ and $y = \frac{2}{5} \triangle = 4 Dq$. Thus each t_{2g} electron is stablised by $-4 Dq$ and each e_g electron is destabilised by $+ 6 Dq$.

The symbol t_{2g} indicates a *triplet orbital degeneracy* i.e. a three fold degeneracy comprising *in this case* the orbitals d_{xy}, d_{xz}, d_{yz}. The symbol e speaks of a *two fold degeneracy* comprising *in the present case* the orbitals $d_{x^2-y^2}$ and d_{z^2} The subscript g stands for 'gerade' or even. In an octahedral complex the metal ion is at the centre of inversion, and with respect to this inversion centre the d-orbitals maintain the same sign of their wave function (i.e. same sign on the lobes) on inversion (Fig. 1.20). But a tetrahedron has no centre of inversion and hence the g subscripts are dropped in a tetrahedral crystal field. The subscript 2 has its origin in group theory and refers to some particular symmetry operations. It may be noted that p orbitals change their sign on inversion in octahedral field and hence they are 'ungerade' or uneven and carry the symbol 'u'.

The splitting of the d-orbitals has significant consequences on the colour and magnetic properties of transition metal complexes. The d-orbital electrons in a crystal field will now have a choice of either going to the t_{2g} or to the e_g set. There will be two opposing forces in this regard. The crystal field splitting $\triangle$
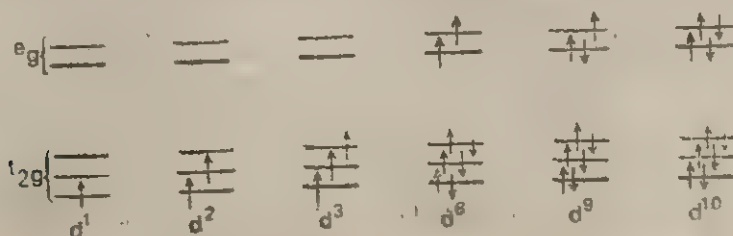
FIG. 10.7. The d^1, d^2, d^3, d^5, d^9 and d^{10} configurations in octahedral field.

(10 Dq) will tend to force as many electrons into the more stable t_{2g} set whereas the electron pairing energy (energy required to cause pairing of two electrons in the same orbital), P, will counter any move to induce spin pairing in the t_{2g} set. In practice the relative magnitude of $\triangle$ (10 Dq), which for a given metal ion varies from ligand to ligand, and P (which is fixed for a given metal ion but varies from metal ion to metal ion) will decide whether or not spin pairing will take place, that is, will decide whether or not the t_{2g} set will be occupied in preference to the e_g set. The d^1, d^2, d^1 systems will occupy the t_{2g} set with their electron spins parallel and this will be true irrespective of the strength of the crystal field. Again d^8, d^9 and d^{10} systems can be arranged in one way only with two, one and no unpaired electrons in the e_g set (Fig. 10.7).

But in the cases of d^4, d^5, d^6 and d^7 *high-spin* (maximum possible number of unpaired electrons) and *low-spin* (minimum possible number of unpaired electrons) may arise. According to Hund's rule of maximum spin multiplicity (Chapter 11) n unpaired electrons will tend to occupy n orbitals to give rise to n unpaired spins. Thus pairing of spin is not normally a favourable process and the pairing energy P will have to be used to counter the electrostatic repulsion between two electrons in the same orbital. A d^4 high-spin system in a crystal field will have three electrons in the t_{2g} set (energy $= 3 \times (-2/5\ \triangle) = -6/5\ \triangle = -12\ Dq$) and one in the e_g set (energy $= 3/5\ \triangle = 6\ Dq$), the total energy due to the crystal field being $-6/5\ \triangle + 3/5\ \triangle = -3/5\ \triangle = -6\ Dq$. On the contrary if the crystal field is strong enough to induce spin pairing, all four electrons will remain in the t_{2g} set and taking the
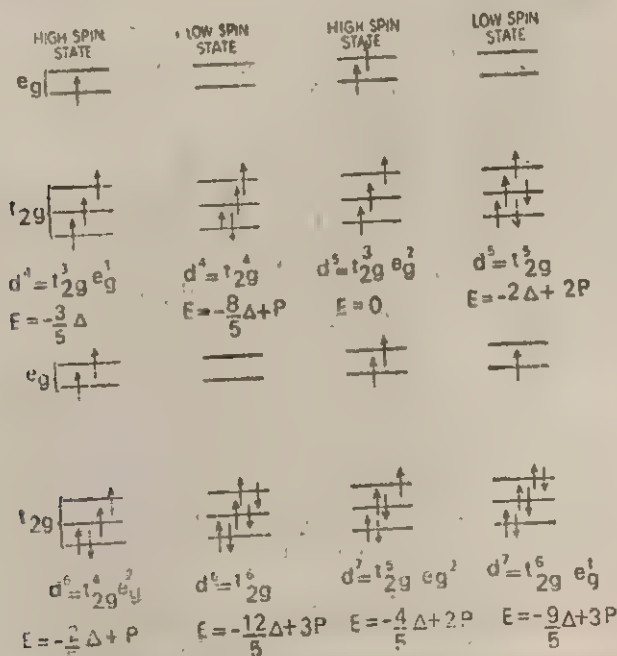
Fig. 10.8. High-spin and low-spin configurations and their energies for d^4, d^5, d^6 and d^7 ions in octahedral field.

pairing energy into consideration, the energy is $4 \times (-2/5\ \triangle) + P = -8/5\ \triangle + P = -16\ Dq + P$. The energies of the d^4, d^5, d^6 and d^7 systems in the two states are enumerated in (Fig. 10.8).

A perusal of the above energy values shows that on putting $\triangle = P$, each of the d^4, d^5, d^6 and d^7 systems provide the same energy for both the spin states. With $\triangle > P$ the energy of the low spin state becomes smaller than that of the high spin state i.e. the low spin state becomes the preferred state. With $\triangle < P$ the reverse holds. This condition for high spin d^6 is demonstrated below:

For the high spin state $\triangle < P$ i.e. $P > \triangle$. So $P = \triangle + x\ \triangle$

Energy of the high spin state $= -2/5\ \triangle + P = -2/5\ \triangle + \triangle + x\triangle$
$(t_{2g}^4\ e_g^2)$ $\qquad = 3/5\ \triangle + x\ \triangle$

Energy of the low spin state $= -12/5\ \triangle + 3P - - 12/5\ \triangle + 3\ \triangle + 3x\ \triangle$
$(t_{2g}^6\ e_g^0)$ $\qquad = 3/5\ \triangle + 3x\ \triangle$

Thus the energy of the low spin state is greater than the energy of the high spin state. Therefore the high spin state will result when $\wedge < P$ and conversely the low spin state will be the ground state when $\triangle > P$. These two conditions are apparent on mere inspection of the energies of the two spin states of d^5 (Fig. 10.8). When $\triangle > P$, the energy of the low spin state is negative while the energy of the high spin state is zero. Again when $\triangle < P$, the energy of the low spin state is positive while the energy of the high spin state is still zero.

Thus the spin state of an ion in a complex depends on whether the crystal field splitting is bigger or smaller than the pairing energy. When $\triangle$ is greater than P, electrons will tend to pair their spins and when $\wedge$ is smaller than P elecrons will tend to remain unpaired and will spread out in the d-orbitals. *A weak field ($\triangle < P$) produces high spin complexes while a strong field ($\triangle > P$) gives low spin complexes. Note also that the spin arrangement in weak field complexes is the same as in free ion, although the orbitals are no longer degenerate.*

For each of d^4, d^5, d^6, d^7 ions there is a *critical crystal field strength* ($\triangle = P$) below which all ligands will produce high spin state and above which all ligands will produce low spin state. The critical $10Dq$ ($\triangle$) is sometimes referred to as the cross-over region (Fig. 10.9). A ligand, whose crystal field strength is close to the critical $10\ Dq$ of a particular d^n ion ($n = 4, 5, 6, 7$), can give rise to spin state equilibrium. The difference in energies of the two spin states around the cross-over region is in the range of thermal energy so that spin state equilibrium may be shifted either towards the high spin state or the low spin state by changing the temperature. Room temperature magnetic moments of tris (dialkyl dithiocarbamato)
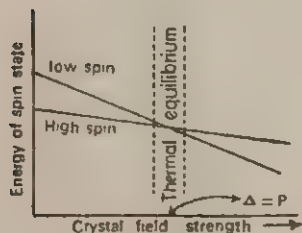
FIG. 10.9. Spin state equilibrium

iron (III) ($3d^5$), $\left(R_2N - C \diagdown \begin{smallmatrix} S \\ S^- \end{smallmatrix} \right)_3$ Fe,
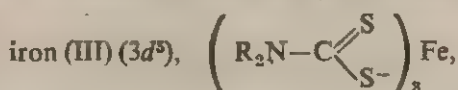
range from $\mu = 5.83$ (R = pyrrolidoyl) io $\mu = 3.02$ B.M. (R=isobutly). Almost any intermediate value can by produced by proper selection of the alkyl group.

In keeping with this spin-state equilibrium increasing pressure gives lower moment. Pressure reduces volume and this is possible only if the more repelling e_g electrons of the high spin form move into the less repelling t_{2g} level giving more of the low spin form. Electrons in the e_g level increase the metal-ligand bond distance. d^1, d^5, d^6 and d^7 ions can give rise to spin state equilibrium with both the forms having the octahedral geometry. For other ions e.g. $3d^8$ Ni (II) *such equilibria must arise out of differing geometries of the two spin states.*

Tetrahedral Complexes: A tetrahedron is best conceived by taking the alternate corners of a cube (Fig. 10.10). The centre of the cube is occupied by the metal ion. The dispositions of the d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$ and d_{z^2} orbitals relative to the tetrahedral points (where we place four ligands) show that d_{xy}, d_{xz} and d_{yz} orbitals
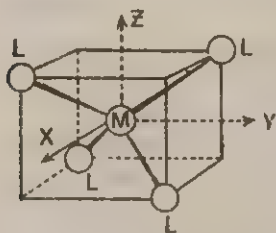
FIG. 10.10. A tetrahedral ML_4 complex with the four ligands at the alternate corners of a cube, the centre of which is occupied by the metal ion.
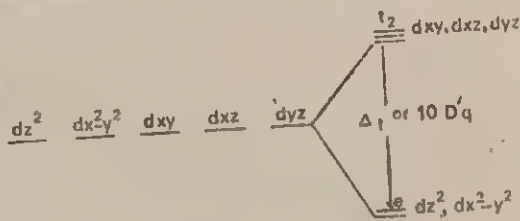
FIG. 10.11. Splitting of the d orbitals in a tetrahedral field.

lie just half an edge of a face of the cube away from the nearest ligands whereas the $d_{x^2-y^2}$ and d_{z^2} orbitals lie half a diagonal of a face of the cube away. For example, each of the two lobes of the d_{z^2} orbital along the z axis will be placed in between the two ligands which occupy diagonally opposite corners of a face of the cube. Thus in contrast to the octahedral geometry, in a tetrahedral crystal field d_{xy}, d_{xz}, d_{yz} orbitals (t_2 set) are repelled more and hence destabilised compared to the $d_{x^2-y^2}$ and d_{z^2} orbitals (e set) (Fig. 10.11). Further, calculations show that for a given metal ion and a given set of ligands and the same internuclear distance the tetrahedral splitting $\triangle t$ is about 4/9th of the octahedral splitting between the same metal ion and the same six ligands. In principle only d^3, d^4, d^5, and d^6 may exist in both spin states. The low spin state will be favoured *only if $\triangle t$ is greater than P*. A tetrahedral field produces only a weak splitting. No tetrahedral field is strong enough to initiate spin pairing ($\triangle t$ *is always less than P*).

Splitting of d-orbitals in other Crystal Fields: In Fig. 10.12 we give the d-orbital ordering in several other fields. In a square planar geometry the $d_{x^2-y^2}$ orbital alone directly faces the four ligands along the x and y axes. Hence $d_{x^2-y^2}$ orbital is the most destabilised. d_{xy} orbital is also repelled by the ligands but expectedly to a lower extent. The d_{xz} and d_{yz} orbitals are not in the immediate vicinity of the ligands. In an idealised square planar stereochemistry there are no ligands along the z direction and thus the d_{z^2} orbital is the most stabilised.

In square pyramidal geometry the $d_{z^2-y^2}$ orbital is face to face with the four ligands in the equatorial xy plane and hence this is the most destabilised orbital. Next in order will be the d_{z^2}, d_{xy}, and the doublet set d_{xz}, d_{yz}. In the trigonal bipyramidal geometry the d_{z^2} orbital is the most destabilised as it faces two ligands

$$ -- \; d_{x^2-y^2} $$
$$ -- \; d_{xy} $$
$$ == $$
$$ ==\; d_{xz}, d_{yz} $$
$$ -- \; d_{z^2} $$

$$ -- \; d_{x^2-y^2} $$
$$ -- \; d_{z^2} $$
$$ ==< $$
$$ -- \; d_{xy} $$
$$ == \; d_{xz}, d_{yz} $$

$$ -- \; d_{z^2} $$
$$ == $$
$$ == \; d_{x^2-y^2}, d_{xy} $$
$$ == \; d_{xz}, d_{yz} $$

SQUARE PLANAR   SQUARE PYRAMIDAL   TRIGONAL BIPYRAMIDAL
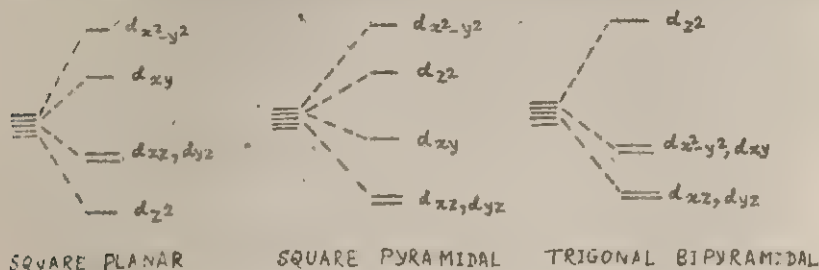
FIG. 10.12. Splitting of the d-orbitals in square planar, square pyramidal and trigonal bipyramidal crystal fields.

directly. However the equatorial orbitals d_{xy}, $d_{x^2-y^2}$ do not face the three ligands (in the xy plane) directly but are equidisposed with respect to them. The d_{xz}, d_{yz} orbitals, as expected, are the most stabilised. In trigonal planar geometry the two ligands along the z axis are missing and hence the d_{z^2} orbital is now the most stabilised orbital. The energy order will be: $d_{z^2-y^2}$, $dxy > d_{xz}$, $d_{yz} > d_{z^2}$. In a linear geometry the z axis is taken as the unique axis and the two ligands are placed on either side of the metal ion. It can be guessed that the energy order is: $d_{z^2} > d_{xz}$, $d_{yz} > d_{xy}$, $d_{x^2-y^2}$

Crystal Field Stabilisation Energy: The stability gained by a d^n ion due to the splitting of its d-orbitals by a crystal field and preferential occupation of the lower energy d-orbitals is called its *crystal field stabilisation energy (CFSE)*. The CFSE provokes the transition metal ions to form complexes with preferred geometries. Thus CFSE of d^7 ion in high spin octahedral stereochemistry ($t_{2g}^5 e_g^2$) is $5(-4\ Dq) + 2(+6\ Dq) = -8\ Dq$ (Table 10.5) compared to the unsplit baricentre. Pairing energy need not be considered for calculation of CFSE but has to be considered for the total energy (Fig. 10.8). CFSE's are useful in interpreting several behaviours of transition metals:

(1) stereochemical preference,

(2) variation of ionic radii (3) thermodynamic properties.

(1) *Stereochemical Preference:* Octahedral low spin cobalt (III) ($3d^6$) has the highest CFSE $= -24\ Dq$. This explains why almost all cobalt (III) complexes are low-spin octahedral. High-spin $[CoF_6]^{3-}$ is the only exception. This is due to the weak crystal field strength of the fluoride ligand, which cannot exceed P ($P =$ pairing energy of Co^{3+}). It is commonly observed that d^3 and d^8 ions prefer octahedral geometry because these ions have high CFSE $= -12\ Dq$. A perusal of Table 10.5 reveals that the difference in CFSE between octahedral and tetrahedral geometries is smaller for cobalt (II) than for nickel (II). Therefore a tetrahedral cobalt (II) complex has a better prospect to be formed in aqueous medium than a tetrahedral nickel (II) complex. In fact addition of excess HCl

to pale pink $[Co(H_2O)_6]^{2+}$ changes the colour to blue due to the formation of tetrahedral $[CoCl_4]^{2-}$ while similar addition to $[Ni(H_2O)_6]^{2+}$ has no effect. The smaller the difference in the CFSE's of the two complexes the greater is the prospect of the reaction to proceed from left to right under the mass action of the weaker chloride ligand:

$$[M(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [MCl_4]^{2-} + 6H_2O$$
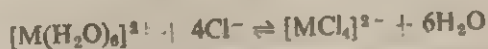
d^0, d^5 (weak field) and d^{10} ions have no CFSE in either octahedral or tetrahedral field. Hence such ions have no preference for any particular stereochemistry on crystal field grounds. In such cases stereochemistry and coordination number are decided by ligand-ligand repulsion, size of the cation and cation charge Zinc (II) $(3d^{10})$ shows a preference for a tetrahedral geometry as this geometry minimises ligand-ligand repulsion by maximising L–M–L angles to 109°.

Table 10.5. CFSE in Octahedral and Tetrahedral Fields

d^n	High-spin octahedral (Dq)	Low-spin octahedral (Dq)	Tetrahedral $(Dq_t) = \frac{4}{9} Dq$
d^1	-4	-4	$-6 = -2.7$
d^2	-8	-8	$-12 = -5.3$
d^3	-12	-12	$-8 = -3.5$
d^4	-6	-16	$-4 = -1.8$
d^5	0	-20	$0 = 0$
d^6	-4	-24	$-6 = -2.7$
d^7	-8	-18	$-12 = -5.3$
d^8	-12	-12	$-8 = -3.5$
d^9	-6	-6	$-4 = -1.8$
d^{10}	0	0	$0 = 0$

That CFSE dictates the stereochemical preference of metal ions is also revealed by an inspection of the structures of *normal spinels* and *inverted spinels*. Spinels are mixed metal oxides, AB_2O_4, where A is a bivalent and B is a trivalent metal ion. Close packing of oxide ions gives both octahedral and tetrahedral holes (page 124). *In normal spinels* the bivalent A ions occupy tetrahedral holes while the trivalent B ions occupy the octahedral holes. In *inverted spinels* the bivalent A ions have moved into the octahedral holes while half of the trivalent B ions have moved out of the octahedral holes to occupy the tetrahedral holes.

Normal spinel
A[BB]O$_4$
example: Mn^{II}[Al$_2^{III}$]O$_4$

Inverted spinel
B[AB]O$_4$
example: Al^{III}[Ni^{II}Al^{III}] O$_4$

The very favourable CFSE $(-12\ Dq)$ of nickel (II) in octahedral geometry leads to the *inverted spinel* structure in NiAl$_2$O$_4$. Aluminium (III) is a $3d^0$ system and has no CFSE. In low spin octahedral state $3d^6$ cobalt (III) has a very high CFSE $(-24\ Dq)$ compared to that of high spin cobalt (II) $(-8\ Dq)$. Although oxide

ion is weak it can still force spin pairing in cobalt (III). Thus Co_3O_4 assumes a normal spinel structure $Co^{II}[Co_2^{III}]O_4$. Iron (III) ($3d^5$) in high spin state has no CFSE but $3d^6$ iron (II) in high spin form has $-4\ Dq$. Hence a stable system results if Fe_3O_4 assumes an inverted spinel structure $Fe^{III}[Fe^{II}Fe^{III}]O_4$. If Fe_3O_4 had assumed a normal spinel structure the stability gain would have been only CFSE of $3d^6$ iron (II) in tetrahedral stereochemistry $(-6\ Dq_t \simeq -3\ Dq)$ compared to $-4\ Dq$ of the inverted structure. Similar reasoning would predict a *normal spinel* structure for Mn_3O_4

(2) *Variation in Ionic radii:* The bivalent metal ions in the high spin metal oxides, MO, are octahedrally surrounded by the weak oxide ions. As we move from Ca^{2+} to Zn^{2+} there is a partial filling up of the t_{2g} level first, then partial filling of the e_g level, then of the t_{2g} level again and so on to give finally $t_{2g}^6 e_g^4$ in Zn^{2+}. An e_g electron repels ligand electrons more than does a t_{2g} electron. Since an e_g electron faces the ligands directly it screens the nuclear charge of the metal ion from the ligands more effectively than the t_{2g} electron. Hence an e_g electron is likely to increase the metal-ligand distance i.e. the $M-O$ bond length while a t_{2g} electron will have the opposite effect. Therefore as we move from $Ca^{2+}(3d^0)$ (t_{2g}^0) through Sc^{2+} (t_{2g}^1), Ti^{2+} (t_{2g}^2), V^{2+} (t_{2g}^3) the ionic radii of M^{2+} gradually decreases to reach a minimum in V^{2+} due to increase in the number of protons in the nucleus with increasing atomic number. The radii (as revealed by the $M-O$ distance) then start increasing with a maximum in Mn^{2+} $(t_{2g}^3 e_g^2)$, then fall again to a minimum in Ni^{2+} $(t_{2g}^6 e_g^2)$ and finally rise again to another maximum in Zn^{2+} (Fig. 10.13).
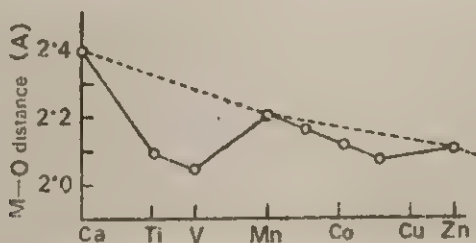
FIG. 10.13. Variation of M^{2+} radii in MO compounds.

Note that the ionic radii of the three ions without any CFSE (Ca^{2+}, Mn^{2+}, Zn^{2+}) lie almost on a line, showing the effect of gradual contraction with increasing atomic number. In Fig. 10.13 $M-O$ distance has been plotted.

(3) *Thermodynamic Properties:* (a) *Hydration Energy:* This is defined. as the heat liberated when one mole of a gaseous metal ion is dissolved in water:

$$M^{2+}(g) + xH_2O \rightarrow [M(H_2O)_x]^{2+}$$

With decrease in ionic radii the hydration energy should increase. Of the d^n ions, d^0, d^5 (high spin) and d^{10} have no CFSE so that the hydration energies of these ions (Ca^{2+}, Mn^{2+}, Zn^{2+}) should be function of their ionic size and should lie on a smooth line. The experimental plot of hydration energies (Fig. 10.14) against atomic numbers gives a double humped curve having the highest values at V^{2+}/Cr^{2+} and Ni^{2+}/Cu^{2+} regions. When these experimental values are corrected for CFSE

by subtracting the relevant Dq's obtained from the spectra of the aquo complexes the corrected values lie on a smooth line connecting the d^n, d^5 and d^{10} ions (Fig. 10.14a).

(b) *Lattice Energy:* This is the heat of the reaction:

$$M^{n+}(g) + n\,X^-(g) \leftarrow MXn,s$$
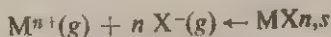
for the case of univalent anions. Once again a double humped curve is obtained when the lattice energies are plotted against atomic numbers. In the absence of any *CFSE* the lattice energies should increase with decreasing ionic radius. A good line is obtained when these lattice energies are corrected for the *CFSE* calculated from optical data of the MX_2 compounds (Fig. 10.14b).

FIG. 10.14. (a) Hydration energies $(-\triangle H)$ of M^{2+} ions; • experimental points; X corrected for CFSE
(b) Lattice energies (-U) of MCl_2 (octahedral coordination of Cl^- ions in the crystal lattice), • Experimental points. The straight line is lattice energy minus *CFSE*.

It is interesting to note that a double humped curve is also produced when the *CFSE*'s (in units of respective Dq's) of weak fields are plotted against atomic number. *CFSE* reaches a maximum $(-12\ Dq)$ in d^3 chromium (III), vanadium (II) and then drops to zero in high spin d^5 manganese (II). It starts rising again reaching a second maximum in d^8 nickel (II) and dropping down to zero again in d^{10} zinc (II).

Variation of 10 Dq:

1. Given the same metal ion and the same geometry it varies from ligand to ligand. This variation gives us the following *spectrochemical series* of ligands in order of increasing crystal field splitting:

$$I^- < Br^- < NO_3^- < Cl^- \sim -SCN^- < F^- < C_2O_4{}^{2-} < H_2O < -NCS$$
$$< EDTA \sim gly < py < NH_3 < en \sim BigH < dipy \sim o\text{-phen} < NO_2{}^- < CN^-$$

2. Given the same metal ion and the same ligand it varies from geometry to geometry:

square planar	octahedral	tetrahedral
13 Dq (oct)	10 Dq (oct)	4.5 Dq (oct)

3. Given the same ligand, the same geometry and the same valence 10 Dq varies from metal ion to metal ion:

M^{2+}	V^{3+}	Cr^{2+}	Mn^{2+}	Fe^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}
10 Dq (kK) of $[M(H_2O)_6]^{2+}$	12.4	13.9	8.5	10.4	9.3	8.5	12.6

4. Given the same ligand, the same geometry, the same metal but varying valence, 10 Dq increases with increasing valence. 10 Dq increases due to substantial increase in σ bonding due to an obvious decrease in the radius of the metal ion. The increased charge will drag the ligands more strongly, thus perturbing the d-orbitals to a greater extent.

$[Mn(H_2O)_6]^{2+}$	$[Mn(H_2O)_6]^{3+}$	$[Cr(H_2O)_6]^{2+}$	$[Cr(H_2O)_6]^{3+}$
10 $Dq(kK)$ 8.5	21.00	13.9	17.4

5. Given the same ligand, the same geometry, the same valence, 10 Dq increases in a group from the first transition series to the second and then to the third. It is likely that the $4d$ and $5d$ orbitals due to their larger size interact better with the ligand orbitals than the $3d$ orbitals. Increased nuclear charge of the metal ions has also an effect.

	$[Co(en)_3]^{3+}$	$[Rh(en)_3]^{3+}$	$[Ir(en)_3]^{3+}$
10 Dq (kK)	24.0	35.0	41.0

Tetragonal Distortion*: This distortion arises from uneven ligation on the equatorial and axial sites of a six-coordinate complex e.g.: trans ML_4X_2. Since the crystal field strengths of equatorial L and axial X are different the t_{2g} and the e_g sets will split further. Taking X as weaker than L it can be seen that the d_{z^2} orbital will be rather stabilised while the $d_{x^2-y^2}$ orbital will be destabilized. Again the d_{xz} and the d_{yz} orbitals (with z components) will be stabilised while the d_{xy} orbital will be destabilised (Fig. 10.15). If the two trans ligands (X) are pulled to infinity an idealised square planar geometry with the d-orbital ordering $d_{z^2} < d_{xz}$, $d_{yz} < d_{xy} < d_{x^2-y^2}$ will result. Whether or not the d_{z^2} orbital will be above or below the d_{xz}, d_{yz} set or the d_{xy} orbital will be decided by the nature of the metal ion and the ligands. The energy gap between the highest two occupied orbitals will dictate the spin state of a complex. Thus the Ni (diamine)$_2$ X$_2$ (diamine = N, N' diethylethylenediamine) complexes are diamagnetic when X = Br or I and paramagnetic when X = Cl or NCS (μ=3.2 B.M.). When the axial and the equatorial ligands are widely different in their donor strengths we get a low spin tetragonal (or square planar) complex while when the difference is not appreciable a high spin tetragonal complex is formed. When the energy separation between the highest two occupied orbitals in a tetragonal complex is close to the pairing energy the complex is likely to exhibit spin state equilibrium. $3d^8$ Ni (II) is a good example.

Fig. 10.15. Tetragonal distortion of an octahedral stereochemistry

When the axial ligands are weaker than the equatorial ligands *tetragonal elongation* (Fig. 10.15) leads to four short metal-ligand bonds on the equatorial plane and two long metal-ligand bonds on the axial plane. Strong metal-ligand interaction in the axial plane gives rise to *tetragonal compression* with short metal-ligand bonds along the axial plane and long metal-ligand bonds on the equatorial

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* Cubic ; $x = y = z$; tetragonal ; $x = y \neq z$; x, y and z represent metal-ligand bond lengths along the specified axes.

plane. The d-orbital ordering then becomes $d_{xy} < d_{xz}$, $d_{yz} < d_{x^2-y^2} < d_{z^2}$. Oxo-vanadium (IV) complexes are good examples of tetragonal compression. In $VO(H_2O)_5SO_4$ the vanadyl oxygen-vanadium bond length is only 1.67A while vanadium aqua oxygen bond lengths along the equatorial plane are $\sim$ 2.3A.

Jahn-Teller Effect: If octahedral complex (ML_6) is assumed to be subjected to some tetragonal distortion the degeneracy of the t_{2g} set and the e_g set may be further lifted. Let us examine the case of high spin d^4 in a tetragonally elongated octahedral geometry (Fig. 10.16). Splitting of the t_{2g} set leads to no extra stability $2 \times (-\frac{1}{3} \delta) + 1 \times (\frac{2}{3} \delta) = 0$, but the e_g electron will gain in stability by $-\frac{1}{2} \delta'$. *It is this gain in stability that motivates the system to undergo distortion.* In the case of d^9 copper (II) once again the system gains no extra stability from the splitting of the t_{2g} set but does gain from the splitting of the e_g set. Indeed many copper (II) complexes are distorted from ideal geometry. An inspection of Fig. 10.16 shows that distortions from ideal octahedral geometry will occur whenever the t_{2g} set or the e_g set is either less than half-filled or more than half-filled. No distortion is

FIG. 10.16. Jahn-Teller splitting of a high spin d^4 complex.

expected when these sets are half-filled or filled. Distortion will occur whenever there is uneven population of the t_{2g} or the e_g set.

Jahn and Teller proposed an important theorem: *Whenever a degenerate orbital state exists in the ground state or the excited state the ion will so distort itself that the degeneracy is lifted resulting in a state of lower energy i.e. higher stability.* In terms of symbols, A (singlet; non-degenerate) term carries no Jahn-Teller effect but E (doublet; two-fold degenerate) and T (triplet; three-fold degenerate) terms do. An explanation of the term symbols appears in Chapter 11. Jahn-Teller effect need not operate in octahedral or tetrahedral complexes unless all the ligands are the same. Mixed ligand complexes are already distorted from idealised geometry because of varying crystal field strengths of the ligands. Table 10.6 lists Jahn-Teller effects in octahedral and tetrahedral complexes.

The t_{2g} electrons do not directly face the ligands in an octahedral field but the e_g electrons do. Uneven population of the e_g orbitals will force a greater disparity in the metal-ligand bond lengths than can be forced by the t_{2g} electrons. The most important examples of Jahn-Teller effect are found in:

d^4 : high spin chromium (II) and manganese (III) ($t_{2g}^3 e_g^1$)

d^7 : low spin cobalt (II) and nickel (III) ($t_{2g}^6 e_g^1$)

d^9 : copper (II) ($t_{2g}^6 e_g^3$)

If the unpaired electron in $3d^9$ copper (II) is in the d_{z^2} orbital metal-ligand bond length in the axial plane will be shorter than those in the equatorial plane.

Table 10.6. Jahn–Teller Effect in d^n Ions in Ground States

Ion	Octahedral Complex high spin	low spin	Tetrahedral complex
d^1	Yes (t_{2g}^1)	—	Yes (e^1)
d^2	Yes (t_{2g}^2)	—	No (e^2)
d^3	No (t_{2g}^3)	—	Yes $(e^3 t_2^1)$
d^4	Yes $(t_{2g}^3 e_g^1)$	Yes (t_{2g}^4)	Yes $(e^2 t_2^2)$
d^5	No $(t_{2g}^3 e_g^2)$	Yes (t_{2g}^5)	No $(e^2 t_2^3)$
d^6	Yes $(t_{2g}^4 e_g^2)$	No (t_{2g}^6)	Yes $(e^3 t_2^3)$
d^7	Yes $(t_{2g}^5 e_g^2)$	Yes $(t_{2g}^6 e_g^1)$	No $(e^4 t_2^3)$
d^8	No $(t_{2g}^6 e_g^2)$	—	Yes $(e^4 t_2^4)$
d^9	Yes $(t_{2g}^6 e_g^3)$	—	Yes $(e^4 t_2^5)$

This is because the nuclear charge of copper (II) is less completely shielded in the z direction than in the x and y directions. Copper (II) thus develops a greater electronegativity in the axial plane than in the equatorial plane. The electron distribution will then be:

$$d^1{}_{z^2} > d^2{}_{x^2-y^2} > d^2{}_{zz}, d^2{}_{yz} > d^2{}_{zy}$$

The reverse will be true if the electron is in the $d_{z^2-y^2}$ orbital. X-ray crystal structure of $CuCl_2$ shows that each copper (II) is octahedrally surrounded by six chloride ions but with different copper-chlorine distance ($4Cl^-$ at 2.30A and $2Cl^-$ at 2.95A) indicating that the unpaired electron is in the $d_{z^2-y^2}$ orbital. The electron distribution then is most likely to be:

$$d^1{}_{z^2-y^2} > d^2{}_{z^2} > d^2{}_{zy} > d^2{}_{zz}, d^3{}_{yz}$$

Hexaaquotitanium (III), a $3d^1$ system, is susceptible to Jahn-Teller distortion both in the ground state and the excited state. Instead of a sharp, single absorption band $(t_{2g} \rightarrow e_g)$ a broad asymmetric band covering several close transitions eg: (tetragonal elongation: $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$; $d_{xz}, d_{yz} \rightarrow d_{z^2}$ etc; tetragonal compression: $d_{xy} \rightarrow d_{z^2}$; $d_{xy} \rightarrow d_{x^2-y^2}$ etc.) is observed.

Two S—O stretches (915 cm^{-1} and 960 cm^{-1}) in the infrared spectrum of $[Mn(DMSO)_6]$ $(ClO_4)_3$ (DMSO = dimethylsulfoxide) indicate differently bonded DMSO molecules. (Free DMSO has S—O stretch at 1055 cm^{-1}). High spin manganese (III) has an uneven distribution of electrons in the e_g orbitals $(d^1{}_{x^2-y^2}, d^0{}_{z^2}$ or $d^0 x^2-y^2, d^1{}_{z^2})$. Since the intensity of the 915 cm^{-1} band is almost double that of the 960 cm^{-1} band, the nuclear screening is less in the square plane giving four strongly oxygen-coordinated DMSO ligands. It has been concluded that the fourth electron is in the d_{z^2} orbital. Instead of a single absorption band $(t_{2g} \rightarrow e_g)$ expected for an undistorted octahedron the complex gives three bands:

$$d_{z^2} \rightarrow d_{x^2-y^2} (14.5\ kK);\ d_{xy} \rightarrow d_{x^2-y^2}\ (17\ kK)\ \text{and}\ d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}\ (20 kK).$$

High spin $[CoF_6]^{3-}$ (d^6) is Jahn-Teller sensitive in the ground state ($t_{2g}{}^4e_g{}^2$) and more so in the excited state ($t_{2g}{}^3e_g{}^3$). Instead of a single absorption band ($^5T_{2g} \rightarrow {}^5E_g$; cf. Fig. 11.11.) a split spectrum (bands at ~ 700 nm and ~ 900 nm) is obtained.

Static Jahn-Teller effect results in a permanent distortion of the complex as in copper (II), high spin manganese (III), and high spin cobalt (III). However if the energy difference between the two possible distortions namely: (1) four long equatorial bonds and two short axial bonds and (2) four short equatorial bonds and two long axial bonds is minimal, the final time average structure may be close to an undistorted octahedron. Such a case is said to arise from *dynamic Jahn-Teller distortion* and is difficult to establish experimentally.

Colour of Coordination Complexes: The colour of complexes originates from two sources: (1) d-d transition and (2) charge transfer transition.

d-d transition: In its ground state the d^1 electron of $[Ti(H_2O)_6]^{3+}$ is in the t_{2g} set. On irradiation with blue-green light of energy equal to the $\triangle$ (493 mμ $= 20,300$ cm$^{-1} = 20.3$ kK) of the hexaaquotitanium (III) ion, the complex will absorb such energy to allow a transition of the t_{2g} electron to the excited e_g set. When we see the complex through transmitted light it appears purple violet. For multielectron system interactions between d-electrons gives rise to many electronic states so that more than one transition is possible (Chapter 11). Quantitative expressions have been derived for spectral transitions on the crystal field model connecting energy of the transition, crystal field strength and interelectronic repulsion. Furthermore quantitative expressions are also available connecting magnetic moments with 10 Dq, which connections were not forthcoming from VB theory.

Charge transfer transition: There are many compounds where either the metal ion is highly oxidising and the ligands are reducing or that the metal ion is highly reducing and the ligands are oxidising. In such cases there occurs transfer of charge (i.e. electron) from the reducing partner to the oxidising partner. The metal ions may or may not possess d-electrons. Common examples are intense purple permanganate (Mn(VII), $3d^-$), brick-red mercury (II) iodide (Hg(II), $5d^{10}$), yellow chromate (Cr(VI), $3d^\circ$), dark red $[Fe(dipy)_3]^2$ (Fe(II), $3d^6$), blood red ferric thiocyanate (Fe(III), $3d^5$) etc.

The selection rules of electronic transitions are:

1. No electronic transition is permitted where the ground state and the excited state have different spin arrangements i.e. have different spin multiplicities. Only those transitions are allowed for which $\triangle S = 0$ i.e. *transitions are permitted between states of the same spin multiplicity.*

2. *Only those electronic transitions are allowed for which $\triangle l = \pm 1$. This selection rule due to Laporte points out that no electronic transitions are allowed for which $\triangle l = 0$ or ± 2. Thus transitions such as $2s \rightarrow 2p$, $2s \rightarrow 3p$, $3p \rightarrow 3d$ are allowed but $3d \rightarrow 3d$, $1s \rightarrow 2s$ or $3s \rightarrow 3d$ are not. No electronic transition can occur merely because of redistribution of electrons in similar orbitals i.e. d-d transitions (such as $t_{2g} \rightarrow e_g$ transition in $[Ti(H_2O)_6]^{3+}$) are forbidden. For quantum mechanical proof of the two selection rules see Appendix III.

Although d-d transitions are forbidden yet the coordination complexes of transition metals are coloured. This indicates that Laporte selection rule must be relaxed in practice. Whenever a complex lacks a centre of symmetry (e.g.: in a tetrahedron) or that odd vibrational effects lead to a change of bond lengths or bond angles there is scope for mixing of metal 3d-orbitals with metal 4p orbitals or with ligand p-orbitals. The pure d-character of the transition metal d-orbitals is then lost and Laporte selection rule is relaxed. A situation arises so that electron transfer from a d-orbital to a p-orbital can occur. Forbidden transitions have low molar extinction coefficients (10 to 200) for six-coordinate complexes and (100—1000) for tetrahedral complexes. In a non-centrosymmetric tetrahedral complex the selection rules are relaxed to a greater extent.

Charge transfer transitions may be either from ligand to metal (L → M) or from metal to ligand (M → L). In such complexes the ligand p-orbitals and metal d-orbitals interact to form M.O.'s. When these M.O.'s are arranged in order of their energy it is found that some M.O.'s have predominantly ligand (i.e. p) character while some M.O.'s retain predominantly metal (i.e. d) character. Laporte selection rule allows $p \rightarrow d$ transition ($\triangle l = +1$) so that charge transfer transitions are allowed transitions with high molar extinction coefficients (10^3 to 10^6). Such transitions are usually high energy transitions and occur in the ultraviolet region. Charge transfer complexes appear coloured to our eyes only when the transitions occur in the near visible region or when the transition in the u.v. has a long tail in the visible. Common examples of L → M charge transfer are mercury (II) iodide, MnO_4^-, CrO_4^{2-} etc. Examples of M → L transition include $[Fe(o\text{-}phen)_3]^{2+}$, $[Fe(dipy)_3]^{2+}$ etc. While d-d transitions can occur only in complexes of transition metal ions with incomplete d-level, charge transfer transitions can occur in both transition metals with incomplete d-level as also in d^0, d^{10} and non-transition metal compounds. Charge transfer transitions are also known as *redox transitions*.

The more reducing M is and the more oxidising L is, the lower is the energy of the M → L charge transfer transition. The absorption maximum of $[Fe(dipy)_3]^{2+}$ occurs at 515 mμ while for $[Ni(dipy)_3]^{2+}$, $[Co(dipy)_3]^{2+}$ the maximum is at still lower wave length range. Iron can be estimated down to 10^{-6} gm/ml via formation of $[Fe(dipy/o\text{-}phen)_6]^{2+}$. The more oxidising M is and the more reducing L is the lower is the energy of the L → M charge transfer transition. Thus iron (III) complexes give more L → M charge transfer transitions than does chromium (III). Most colorimetric analyses of trace quantities of metal ions utilise charge transfer transitions. d-d transitions, being of low intensity, are of little value for such purposes.

Charge transfer spectra need not be restricted to M ⟶ L or L ⟶ M type. A third less common type is exhibited by the so-called Prussian blue or Turnbull's blue precipitate K Fe Fe(CN)$_6$. One of the two irons is Fe(III) while the other is Fe(II). Electron transfer is possible from Fe(II) to Fe(III). Note that K$_2$FeFe (CN)$_6$ is colourless because both the irons are Fe(II) and thus there exists no scope for any (redox) charge transfer transition. Given below are the salient distinctions between d-d transitions and charge transfer transitions.

d-d transition	*charge transfer transition*
1. Presence of d electrons essential	1. Presence of d electrons not essential. It may occur in d^0, d^n, d^{10} systems.
2. Laporte forbidden	2. Laporte allowed
3. Low molar extinction coefficient (5-200)	3. Extremely high molar extinction co-efficient (5,000 $\sim$ 35,000)
4. No redox system involved	4. Redox system essential
5. Not useful for spectrophotometric estimation of metal ions	5. Very useful for spectrophotometric estimation of metal ions

More on the electronic spectra from the viewpoint of the crystal field theory is given in Chapter 11.

Passage of Crystal Fields to Ligand Fields: The crystal field model does not consider any covalent interaction between ligands and the metal ion. Experience shows that in several instances overlap of orbitals of the metal ion and the ligands does occur. (1) In a low-spin hexachloroiridium (IV), $[IrCl_6]^{2-}$ (t_{2g}^5) the single unpaired electron has been shown from an analysis of the electron spin resonance spectrum to be delocalised into the six chloride ions. The multiband ESR spectrum convincingly proves that the iridum unpaired electron is definitely disturbed by the nuclei of the chloride ligands. This is not possible unless there occurs an overlap of metal—ligand orbitals. For details on the ESR evidence see Appendix V (2) Intensities of the forbidden $d-d$ transition cannot be adequately explained on the basis of mixing of metal d and metal p/s orbitals alone or on the basis of vibrations of the complex but that metal d-orbitals have to be assumed to be mixed up with ligand p-orbitals also. (3) Crystal field spectral bands cannot be fitted precisely if the interelectronic repulsion of metal electrons in a complex be assumed to be the same as in the free ion (section 11.10.5). Instead, good fits are obtained when the interelectronic repulsion is assumed to be 20-25% less in a complex than in a free ion. It follows that the d-orbitals have expanded in size and have penetrated into ligand orbitals so that repulsions between metal d-orbitals becomes smaller than in the free ion. The ligand electrons partially screen the d-orbital electrons from the nuclear charge of the metal ion. Thus the d-orbital electrons spend sometime on the ligands i.e. metal d-electrons are partially delocalised into ligand orbitals. The average distance between d-orbitals thus increases. This influence of ligands in expanding the d-electron clouds is *known* as *nephelauxetic effect* ('cloud expanding'). Taking β as the ratio of the interelectronic repulsion parameter B' in a complex to B in a free ion, common ligands can be arranged in the following nephelauxetic series: β. free ion $>$ F$^-$ $>$ H$_2$O $>$ NH$_3$ $>$ NCS$^-$ $>$ Cl$^-$ $>$ CN$^-$ $>$ Br$^-$ $>$ S^{2-} $>$ I$^-$. β is $\simeq$ 1 for F$^-$ and 0.25 for I$^-$. Covalent complexes have low β. (4) Antiferromagnetism in metal complexes arise out of metal-metal bonding or via super-exchange through oxygen or fluorine bridges. In the case of super exchange partial spin quenching of the metal ion occurs through filled π-orbitals of the bridging atoms. It may so happen that one of the two electrons of the bridging atom moves into the orbitals of the metal ion which carries the unpaired electron. In order to keep the Pauli principle

valid, ie migrating electron of the bridging atom must have its spin in opposition to that of the metal ion electron (Fig. 10.17). As the other electron of the bridging atom moves into the d-orbital of the second metal ion the spin of the unpaired electron should be aligned opposite to that of the entering π-electron of the bridging atom. Thus the phenomenon of antiferromagnetism through super exchange is a proof of overlap of metal-ligand bonds.
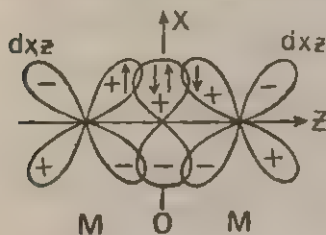
FIG. 10.17. Antiferromagnetic interaction via super exchange (π-bonding): MO oxides

Crystal field model is strictly valid for *ionic* complexes. For highly covalent complexes we have to have recourse to the molecular orbital theory of coordination complexes. All intermediate interactions are covered by *ligand field theory*, which has also been termed as adjusted crystal field theory. In ligand field theory interelectronic interaction parameters such as interelectronic repulsion, spin-orbit coupling constant are taken as ~ 75% of the free ion value. These parameters are essential for quantitative evaluation of magnetic properties and spectral properties of complexes.

10.11.3. A Critique of Crystal Field Theory and Valence Bond Theory: The two theories are based on very widely different premises. Yet for the benefit of the young inquisitive readers some of the salient points are given below:

1. In order to create a required geometry for the metal complex the VB theory hybridises suitable metal orbitals, sometime belonging to different principal quantum numbers. On the contrary the CF theory invokes no mixing of the metal orbitals. Instead, a stereochemistry is assumed, the ligands are placed at these stereochemical positions and then the energetics and hence the distribution of the metal ion d-electrons in the five d-orbitals are examined.

2. VB theory, of necessity, has to promote some d-electrons to higher quantum shells particularly in the cases of d^7, d^8 and d^9 ions in inner orbital octahedral cases. CF theory does not have to do this but merely reorganises the available d-electrons in the t_{2g} and e_g levels (of the same quantum shell), although they are not equi-energetic.

3. The VB theory assumes overlap of filled ligand orbitals with empty hybrid orbitals of the metal ion i.e. covalence is assumed. But C.F. does not accept any overlap between metal and ligand orbitals i.e. complexes are regarded as ionic.

4. The 'outer orbital' and 'inner orbital' octahedral complexes in VB terminology become 'high spin' and 'low spin' complexes in CF terminology.

5. In the "inner orbital" case VB theory uses the $d_{x^2-y^2}$ and d_{z^2} in the hybridisation and hence does not permit d-electrons to be placed in these orbitals. In CF theory these two d-orbitals form the doublet e_g set and because of their higher energy (compared to the triplet t_{2g} set) disfavours putting d-electrons in this set.

6. The explanation of colour of coordination complexes in the low energy visible range is understandable on the CF theory as being due to electron transition

fi :m the lower energy t_{2g} set to the higher energy e_g set (in the simplest cases). However this has to be carried in our minds that such d-d transitions are Laporte forbidden. The VB theory does not have any such simple explanation.

7. CF theory readily admits a gradual transition from high spin octahedral to low spin octahedral or even square planar stereochemistry with increasing donor strengths of the ligands. But VB theory is not suitable for such changes.

8. As a consequence of recognition of the aforesaid gradual change the CF theory offers a satisfactory explanation of the cross over region and spin state equilibrium (leading to anomalous magnetic moments). The VB theory is unable to tackle such situation.

9. The CF theory offers interesting explanation of orbital contribution to spin magnetic moments (cf: 11.12.2) while VB theory fails to provide desired answers.

10.12. STABILITY CONSTANTS

Quantitative study of the formation of a complex offers very useful informations. A complex ML_x may be formed in a number of consecutive steps:

$$M + L \rightleftharpoons ML; \qquad k_1 = [ML]/[M][L]$$

$$ML + L \rightleftharpoons ML_2; \qquad k_2 = [ML_2]/[ML][L]$$

$$\vdots \qquad\qquad\qquad \vdots$$

$$ML_{x-1} + L \rightleftharpoons ML_x; \qquad k_x = [ML_x]/[ML_{x-1}][L]$$
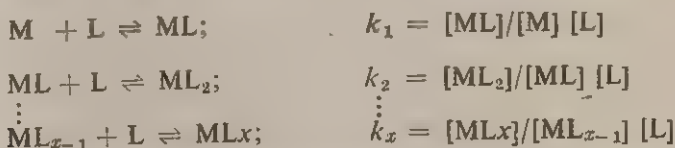
where $k_1, k_2 \ldots k_x$ are the stepwise formation constants. The overall formation (stability) constant may be represented as:

$$M + xL \rightleftharpoons ML_x; \quad K = \frac{[ML_x]}{[M][L]^x}$$

Reciprocal of the stability constant is called instability constant. The symbols β_x are often used to indicate the xth overall formation constant. Thus $\beta_1 = k_1$; $\beta_2 = k_1.k_2$; $\beta_3 = k_1.k_2.k_3$. In aqueous medium the formation reactions involve replacement of the coordinated aqua molecules in the first sphere of attraction by the ligand molecules:

$$[M(H_2O)_6]^{n+} + xL \rightleftharpoons [M^{n+}L_x] + 6H_2O$$

Since the determination is made in the solvent water ([H_2O] = 55 M)] which is present in a constant and very high concentration, the release of coordinated water molecules has insignificant impact on the value of K, and hence the reaction is considered without the solvent molecules.

Starting with a known concentration of the metal ion and the ligand it is possible to determine the concentrations of all the different species involved in the equilibrium. Largely due to the efforts of Bjerrum, Sillen, Calvin, Irving and Schwarzenbach several methods, namely potentiometry, spectrophotometry, polarography, solvent extraction, etc. are now available for the evaluation of

stability constants. A comparative study of the stability constants (Table 10.7) of metal complexes with different ligands provides interesting conclusions:

Table 10.7. Stability Constants (log K) for Metal Complexes in Aqueous Medium

Ligand	K_n	Mn²⁺	Fe²⁺	Co²⁺	Ni²⁺	Cu²⁺	Zn²⁺
				Log Kn			
	K_1	...	...	2.11	2.79	4.15	2.37
	K_2	...	...	1.63	2.24	3.50	2.44
NH₃	K_3	...	...	1.05	1.73	2.89	2.50
	K_4	...	...	0.76	1.19	2.13	2.15
	K_5	...	...	0.18	0.75	−0.52	...
	K_6	...	...	−0.62	0.03	...	...
Ethylene	K_1	2.73	4.28	5.89	7.52	10.55	5.71
diamine	K_2	2.06	3.25	4.83	6.28	0.05	4.66
	K_3	0.88	1.99	3.10	4.26	−1.00	1.72
Salicyladehyde	K_1	3.73	4.22	4.67	5.22	7.40	4.50
	K_2	3.06	3.40	3.63	3.97	5.91	3.60
Ethylenediamine tetraacetic acid	K	14.0	14.3	16.3	18.6	18.8	16.5

(1) The successive formation constants of a complex between a given metal ion and a given ligand steadily fall off (from K_1 to K_6 for metal ammines). This is due to the fact that as more and more ligands move into the coordination zone, less and less aqua molecules are available to fresh ligands for replacement. With progressive intake of ligands the metal ion becomes less electron greedy.

(2) For a given metal ion the formation constants are far larger for a chelating ligand than for a similar non-chelating ligand. This enhanced stability is called *chelate effect*.

When a metal chelate is formed by the displacement of unidentate ligands there is an increase in the disorder of the system because of release of more mole-

$$[M(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [M(NH_3)_6]^{2+} + 6H_2O$$
$$[M(H_2O)_6]^{2+} + 3en \rightleftharpoons [M(en)_3]^{2+} + 6H_2O$$
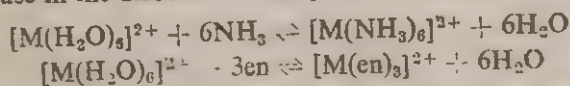
cules. The free energy change of a system, its enthalpy change and entropy change in the standard state are related as

$$\Delta G° = \Delta H° - T\Delta S°$$

Again equilibrium constant of a reaction indicates the standard free energy change in the reaction i.e.

$$\Delta G° = -RT \ln K$$

Thus a lower value of $\Delta G°$ indicates a higher value for K. Enthalpy change between chelated and non-chelated structures is small due to similar metal-donor

atom linkages. It follows from the above relations that more positive value of $\triangle S°$ will lead to more negative $\triangle G°$ and hence a more stable complex will be formed. The chelate effect is thus mainly an entropy effect resulting from an increase of molecules in the system. Following Sidgwick the explanation of the chelate effect may be presented more pictorially. If one of the two metal-ligand bonds of a bidentate chelate system is broken, the remaining bond will still hold the molecule in place, so that the broken link can be reestablished. But a ligand bound by a single link will drift away if the bond is broken. In essence a chelate complex dissociates less than a non-chelated complex and hence registers a higher stability constant.

(3) An empirical order of the stability constants of metal complexes emerges as:

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

This order is commonly known as Irving-Williams series of stability constants. Recent determinations of formation constants of oxovanadium (IV), VO^{2+}, have shown that complexes of this ion are even stabler than those of copper (II).

Several workers have tried to correlate the formation constant data with fundamental properties of metal ions, namely ionisation potential, electronegativity, atomic number, ionic size as also with the basic properties of the ligands. It may be generally stated that stability constants of complexes increase with increasing ionisation potential of the metals (first plus second potentials for M^{2+} ions). Stability constants of a given metal ion for a series of ligands increase with decreasing K_A values of the ligands. Although data on complexes of the second and third transition series are scanty, there is little doubt that the stability constants increase within any group (of transition metals) in passing from the first to the second and to the third series. For example, complexes of nickel (II), palladium (II) and platinum (II) show an increase in thermodynamic stability in that order ($Ni^{2+} < Pd^{2+} < Pt^{2+}$).

10.13. OUTER SPHERE COMPLEXES

Over and above the forces that hold together a given metal ion and certain ligands in the first sphere of attraction in a complex, there exists a weaker interaction between the complex ion and the (counter) ions outside the complex zone. Thus hexammine cobalt (III) ion can hold a chloride ion to give an ion-pair ($[Co(NH_3)_6]^{3+}, Cl^-)^{2+}$. The descriptive name, outer-sphere complex, as against the usual inner sphere complex has been given to such ion-pairs. From accurate physical measurements (conductance, optical density, etc.) it is possible to evaluate formation constants (also called association constants) of outer sphere complexes. Such constants, however, are far lower compared to formation constants of inner sphere complexes. Outer sphere association constants decrease with decreasing charge of the ions and with increasing size of the ions, the charge effect being more important than the size effect (Table 10.8).

Table 10.8. Association Constants for Outer Sphere Complexes

Ion-Pairs	K_A	Ion pairs	K_A
$[Co(NH_3)_6]^{3+}$, Cl^-	74	$[Co(BigH)_3]^{3+}$, Cl	55
$[Co(NH_3)_6]^{3+}$, I^-	17	$[Co(BigH)_3]^{3+}$, Br^-	33
$[Co(en)_3]^{3+}$, Cl^-	52	$[Co(BigH)_3]^{3+}$, I^-	22
$[Co(en)_3]^{3+}$, I^-	9	$[Co(BigH)_3]^{3+}$, SO_4^{2-}	1.6×10^3
$[Co(NH_3)_5Cl]^{2+}$, Cl^-	10		
$[Co(en)_3]^{3+}$, SO_4^{2-}	2.8×10^3		

10.14. FACTORS THAT INFLUENCE COMPLEX FORMATION

The following factors are important in complex formation:

1. *Nature of the central metal ion:* It is a special property of d-electrons, that is, of transition metals that they form stable complexes. The splitting of the d-orbitals in a crystal field provides crystal field stabilisation energy (for d^1 it is -4 Dq; d^2, -8 Dq; for low-spin d^6, -24 Dq etc in octahedral field) whereby the system is stabilised through complexation. The order of stability constants also indicates a preference of a given ligand for metal ions. Ionisation potential, ionic size, electronegativity also influence complex formation. In general complexation is favoured by increasing ionisation potentials, decreasing ionic size and increasing electronegativity of the metal ions. High ionisation potential means the resulting metal ion is quite electron greedy i.e. has a high electronegativity. Such a metal ion obviously will interact better with the lone pair of the ligand.

2. *Nature of the ligands:* Common ligands possess lone pairs of electrons whereby they serve as donors. Electropositive groups are immediately ruled out as ligands. Ligands containing electronegative atoms (with lone pairs), such as carbon, nitrogen, oxygen, sulphur or the halogens are the most useful donors. Too strongly electronegative donors will form weaker complexes since such donors will tend to retain a considerable share of the lone pair on to themselves. Stability constants reflect the influence of the donor atoms.

Negative groups (IO_6^{5-}, TeO_6^{6-}) with a central atom in a high oxidation state stabilises highest oxidation states. Electron deficient ligands (CO, CNR, NO) with vacant orbitals to receive back donated electrons (from metals) are known to stabilise low oxidation states.

3. *Ring Formation:* Polydentate ligands can hold on to the metal ion at more than one point and thus give stabler complexes (*chelate effect*). A chelate complex has a higher stability constant than a non-chelated complex. Thus ring formation by a chelating ligand at the metal ion helps in the formation of a stable complex.

4. *Role of solvent:* Solvent always plays an important role in the synthesis of a particular complex. The chosen solvent must be a weaker ligand than the ligand whose complex is to be synthesised. For example, halide ions are decidedly weaker ligands than water. Therefore syntheses of halo complexes $[NiCl_4]^{2-}$, $[CoCl_4]^{2-}$, etc are carried out as a rule in non-aqueous solvents like alcohol.

5. *Role of pH*: It is a general rule that complexation of a metal ion by a ligand increases with decreasing hydrogen ion concentration, that is, with increasing pH. A metal ion and a hydrogen ion are mutual competitors for a ligand. In presence of a large excess of H^+ the ligand tends to form a proton complex rather than a metal complex. This is illustrated with the salicylaldelyde complex (10-XIX).

(10 XIX)
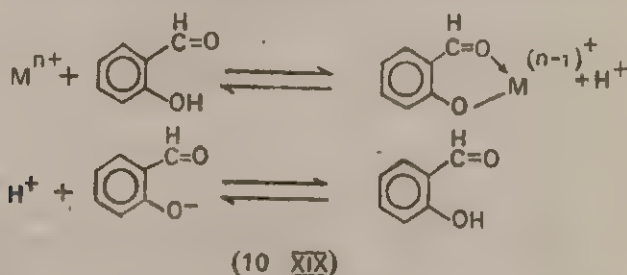
10.15. LESS FAMILIAR OXIDATIONS STATES AND THEIR STABILISATION

Oxidation state may be defined as the atomic number of the atom minus the number of the orbital electrons i.e. as the net charge on the atom. A more rigorous definition runs as: *Oxidation state is the formal charge left on an atom when all the ligands are removed in their closed shell configuration and any element—element bond, are cleaved homolytically.*

d-Block transition elements have incompletely filled *d*-orbitals. Chemical reagents of varying effectiveness can disturb these *d*-orbital electrons to varying extent. These ions can therefore exhibit more than one valence. Less familiar oxidation states commonly mean the oxidation states other than those of commercial availability. Oxidation states of most elements of the first transition series are given in Table 10.9. The double underlined states are the most stable and

Table 10.9. Oxidation States of First Transition Series Elements

	+7	+6	+5	+4	+3	+2	+1	0	−1	−2
Titanium				+4	+3	+2		0	−1	
Vanadium			+5	+4	+3	+2	+1	0	−1	
Chromium		+6	+5	+4	+3	+2	+1	0		
Manganese	+7	+6	+5	+4	+3	+2	+1	0	−1	
Iron		+6		+4	+3	+2	+1	0		−2
Cobalt				+4	+3	+2	+1		−1	
Nickel				+4	+3	+2	+1	0		
Copper					+3	+2	+1			

the single underlined states come next in stability. Exploring the chemistry of these metal ions in less familiar oxidation states has been a fascinating pastime of synthetic inorganic chemists. From such studies some generalisation regarding stabilisation of less familiar oxidation states have now emerged. Complex formation has played a significant role in this area, providing a protective shielding to the new oxidation state against the rigours of oxidation or reduction by the environment.

10.15.1. High Oxidation States: When a metal ion occurs in an oxidation state higher than the one of common occurrence the ion will tend to oxidise its immediate surroundings and would tend to revert to its normal valence.

Metal ions become more acidic (electron greedy) as the valence increases. (1) It is therefore commonly observed that higher oxidation states are frequently formed and stabilised in alkaline medium. Anodic oxidation of iron or ferric hydroxide in concentrated alkali converts $+3$ iron to $+6$ iron (ferrate ion, FeO_4^{2-}) (2) Negative groups containing a central atom of high oxidation number have been found to stabilise high oxidation states. Thus periodate IO_6^{5-} and tellurate TeO_6^{6-} ions have the iodine and tellurium in their highest oxidation number, namely $+7$ and $+6$ respectively. These ions have stabilised silver (III) in M^1_7 $[Ag(IO_6)_2]xH_2O$, $M^1_9[Ag(TeO_6)_2]xH_2O$ and copper (III) in $M^1_9[Cu(TeO_6)_2]xH_2O$. It is interesting to note that these compounds are obtained in an alkaline medium. Quadrivalent nickel has also been stabilised as $Na(K)$ $[NiIO_6]xH_2O$. (3) Higher oxidation states have also been arrested in the form of stable complexes with organic ligands. A suitable organic ligand for such purpose will be one that will withstand any oxidation by the oxidising agent itself or by the higher oxidation state of the metal ion. Bipositive silver has been obtained as inner metallic complexes with pyridine carboxylic acids, eg: $[Ag(Pic)_3]$ (PicH = picolinic acid) or as cationic complex with pyridine $[Ag(py)_4]^{3+}$, with dipyridyl $[Ag(dipy)_2]^{3+}$, with o-phenanthroline $[Ag(o-phen)_3]^{3+}$ etc. All these organic ligands are stable to persulphate ion, which is used in the synthesis to oxidise silver (I). The ligands are also stable to silver (II).

Silver (III) has been stabilised by the quadridentate ligand ethylenedibiguanide (29-VII). Manganese (III) and manganese (IV) have also been stabilised by biguanide and ethylenedibiguanide (29-VII). In general ligands with strong σ-donor abilities (eg: dipyridyl, o-phenanthroline, periodate, fluoride) stabilise higher oxidation states.

10.15.2. Low Oxidation States: In order to save the low oxidation states from oxidation by atmospheric oxygen, syntheses of such oxidation states are often carried out in inert nitrogen atmosphere. Sometimes special handling techniques are also required. Special solvents (completely deaerated) like tetrahydrofuran, dichloromethane, anhydrous alcohols are used.

Most fascinating, however, is the role of the organic ligands which do the stabilisation. The ligands must possess certain special features. (1) Ligands should possess reducing qualities such that a low oxidation state can survive in

its surroundings. CO, NO, CNR, PR$_3$, etc appear reasonable choices. (2) Bonds between ligands and metal ions are formed by electron donation from filled ligand orbitals to empty acceptor orbitals of metal ions. If the metal ion is in a high oxidation state, such electron donation leads to substantial charge neutralisation. On the contrary, if the metal ion is in a low oxidation state ($+1, 0, -1$, etc) electron donation from the ligand will result in accumulation of negative charge density on the metal. Such negative charge build-up will work against the formation of low oxidation states. However ligands like CO, NO, CNR, PR$_3$, etc have empty π-type orbitals (Chapter 5) which can receive back donated electron density from suitable filled orbitals of low oxidation state metal. Such bonding mechanism is synergic, that is, pushing electron density by the metal into the ligand orbitals, makes the otherwise poor donor ligand a far better donor. Thus electron deficient molecules with π-orbitals available for receiving electron density will stabilise low oxidation states. In addition to the ligands already mentioned simple aromatics

Table 10.10. Stabilisation of Low Oxidation States

Metal	Oxidation State	Ligands	Complex
Cr	0	CO	$[Cr(CO)_6]$
	0	CNR	$[Cr(CNR)_6]$
	0	C$_6$H$_6$	$[Cr(C_6H_6)_2]$
	+1	C$_6$H$_6$	$[Cr(C_6H_6)_2]^+$
Fe	0	CO	$[Fe(CO)_5]$
Co	0	CO	$[Co_2(CO)_8]$
	−1	CO	$Na[Co(CO)_4]$
Ni	0	CO	$[Ni(CO)_4]$
	0	CNR	$[Ni(CNR)_4]$
	0	PCl$_3$	$[Ni(PCl_3)_4]$

like benzene, toluene, dipyridyl and cyclopentadiene, ethylene, acetylene all have been found to stabilise low oxidation states very effectively. All these organic ligands are electron deficient molecules so that they can receive backdonated electrons from low valent metals. Some examples of low oxidation state stabilisation are given in Table 10.10.

10.16. THE USES OF COORDINATION COMPLEXES IN ANALYTICAL CHEMISTRY

10.16.1. A Brief Survey: Profound changes occur in the properties of a metal ion on complex formation. These changes are generally reflected in solubility, colour, stability, magnetic properties etc. Some of these changes in properties can be used to a great advantage for analytical purposes. The applications of of complexes in analytical chemistry can be broadly classified under the following heads:

1. *Use of insoluble inner metallic complexes in gravimetric estimation:* Inner metallic complexes of the first order are often insoluble in aqueous medium but may be quite soluble in suitable organic solvents. The formation of such chelates often require suitable pH range and provided such pH ranges are maintained many metal ions can be precipitated quantitatively from their aqueous solution and the metal ions estimated gravimetrically after proper drying. Some common applications include estimation of nickel (II) as red coloured bis (dimethylglyoximato) nickel (II) (10-XX) in slightly ammoniacal medium, of aluminium (III) as yellow coloured tris (8-hydroxyquinolinato) aluminium (III) (10-XXI) in slightly ammoniacal medium, of copper (II) as light green coloured bis (quinaldinato) copper (II) (10-XXII) in dilute sulphuric acid or as dull green bis (salicylaldoximato) copper (II) (10-XXIII) in dilute acetic acid. Not all complexes are stable at the drying temperature (120—150°C), and such complexes are ignited to metal oxides. Examples are complexes of cupferron (10-XXIV), ammonium salt of N-nitroso N-phenyl-hydroxylamine.
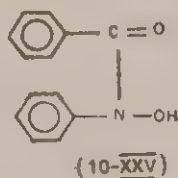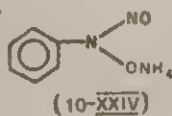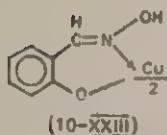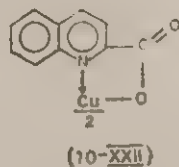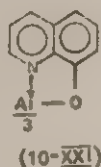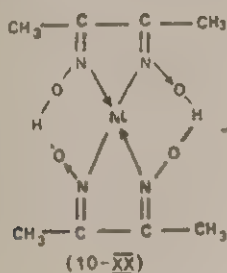
Poor keeping qualities of cupferron and poor stability of its complexes led to a sustained search for a better ligand of the phenylhydroxylamine group. Out of these efforts came N-benzoyl-N-phenylhydroxylamine (BPHAH). This reagent (10-XXV) is more stable to heat and light, less sensitive to pH changes and furthermore its complexes are very stable and are directly weighable. Originally proposed for the gravimetric estimation of Cu(II), Fe(II), TiO(II), Al(III) it has been used, of late, for a variety of metal ions like Sn (II), Th(IV), Nb(V), Ta(V), Be(II) etc. The effective pH ranges of precipitation for copper (II) is 3.6-6.0, for iron (III) 3.0-5.5 and for aluminium 3.6-6.4. These precipitates have definite composition $M(BPHA)_2$ ($M = Cu^{2+}$) and $M(BPHA)_3$ ($M = Al^{3+}, Fe^{3+}$). These can be dried at 100°C and weighed. Beryllium (II) is precipitated at pH 5.5-6.5, dried and weighed as $Be(BPHA)_2$. This reagent has provided a long sought solution to the problem of separation of Nb and Ta. Niobium is precipitated at pH 3.5-6.5 from a tartrate solution and in the filtrate tantalum is precipitated after adjustment of pH to 1. In both these cases the precipitate is ignited to the oxide M_2O_5 and weighed,

2. *Solvent extraction and separation of a metal ion through complexation:* Both iron (III) and aluminium (III) form first order inner complex with 8-hydroxyquinoline. Whereas the tris (8-hydroxyquinolinato) iron (III) is formed over a wide pH range 2 to 10, the tris (8-hydroxyquinolinato) aluminium (III) is formed in slightly ammoniacal medium. Furthermore the iron (III) complex is readily soluble in chloroform. Therefore iron (III) can be separated from aluminium (III) around pH 3.0 by the addition of 8-hydroxyquinoline, followed by extraction with chloroform. The optical density of the chloroform extract is measured at 470 mμ, (1 mμ = 10A) and iron content found out after comparing with a standard iron (III) sample. After extraction of iron, aluminium may be quantitatively estimated in the aqueous phase as tris (8-hydroxyquinolinato) aluminium (III) in slightly ammoniacal medium.

3. *Spectrophotometric estimation of trace quantities of metal ions:* Many transition metal ions form complexes which are very intensely coloured. Several of these intensely coloured species have extremely high absorption so that trace quantities of such metal ions can be accurately determined by measuring the optical density of the complex at optimum wave length. For example, iron (II) forms dark red tris (dipyridyl) iron (II) or tris (o-phenanthroline) iron (II) complexes over a wide range of pH 2—9. Trace quantities (2-10 parts per million; $\sim 10^{-6}$ gm/ml) or iron (II) can thus be determined by measurement of optical density at 515 mμ. The common blood-red colouration that iron (III) develops with excess thiocyanate in acid medium (0.05 $\sim$ 0.5M HNO_3) contains the ion $[Fe(SCN)]_6^{3+}$. Optical density measurements can be carried out at 480 mμ and compared with a standard.

The above mentioned colours are due to charge transfer transitions which are Laporte allowed and hence are of extremely high extinction coefficients. *d-d* transitions are Laporte forbidden, are weak and hence are of little value for spectrophotometric estimation of metal ions.

4. *Complexometric titration:* The sequestering effect of ethylenediaminetetraacetic acid (Table 10.1) has led to the development of some most powerful volumetric methods of estimation of metal ions. EDTA rapidly and strongly complexes metal ions such as Ca^{2+}, Mg^{2+}, Fe^{3+}, Cu^{2+} and so on. In order that a titrimetric end-point be feasible some coloured dyestuff, which itself can form a complex with the metal ion to be titrated, is chosen. Eriochrome Black T(10-XXVI) has a blue colour at pH 10, where Mg^{2+}, Ca^{2+} readily react with EDTA to form the colourless EDTA complexes, $[Mg(EDTA)]^{2-}$ or $[Ca(EDTA)]^{2-}$. Eriochrome Black T complex of Ca^{2+} or Mg^{2+} is much less stable to dissociation (low stability constant) than the metal-EDTA complex.

Eriocrome Black T (1—(1-hydroxy-2 naphthyl azo)-6 nitro —2 naphthol —4 sulphonate)

Moreover the Ca^{2+} and Mg^{2+} complexes of the indicator dye are coloured purple as against the blue colour of the free indicator ion at the pH of titration (10).

The Ca^2/Mg^{2+} solution is buffered to pH 10, a few drops of the indicator dye added and the solution titrated with a standard solution of the disodium salt of EDTA. The EDTA first complexes the free Ca^{2+}/Mg^{2+} available in the solution and then with the Ca^{2+}/Mg^{2+} complex of the indicator dye. Finally the free dye is released, the endpoint being marked by a change from purple to blue. Such complexometric titrations have made water hardness titrations an easy affair compared to the old and laborious palmitate titrations.

5. *Use of organic sequestering agents in removal of interference in gravimetric estimations:* An organic ligand may react with more than one metal ion to form sparingly soluble precipitates. In such cases direct estimation of a particular metal ion in the presence of interfering ions is not feasible. A strong sequestering agent like EDTA has been of immense value in rendering the interfering ions ineffective, and making the precipitating organic ligand nearly specific for a particular ion.

Benzimidazole forms an insoluble silver salt (10-XXVII) in ammoniacal medium, which is granular, readily filterable and insensitive to light. Unfortunately

(10-XXVII)
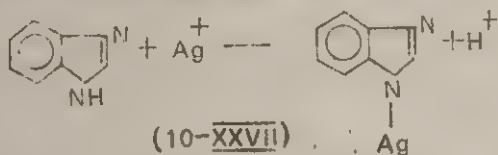
the organic ligand also offers insoluble precipitates with many other ions like Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, etc in ammoniacal medium. But in the presence of EDTA these interfering ions form highly stable and soluble EDTA-complexes, and become indifferent to benzimidazole. Silver however still continues to be precipitated quantitatively.

In the presence of EDTA, beryllium may be precipitated with ammonia in presence of aluminium, bismuth, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, zinc and small amounts of vanadium. Titanium interferes and must be removed.

6. *Qualitative detection of metal ions:* The basis of qualitative detection of metal ions is the quantitative reactions of such ions. Common examples of qualitative detection of metal ions by way of complexation reactions include detection of nickel (II) in group IIIB as red coloured bis (dimethylglyoximato) nickel (II), of cobalt (II) in group IIIB as blue coloured tetrakis (isothiocyanato) cobalt (II), $[Co(NCS)_4]^{2-}$, of copper (II) in group IIA as blue coloured tetrammine copper (II), $[Cu(NH_3)_4]^{2+}$, of iron (III) in group IIIA as blood red hexakis (isothiocyanato) iron (III), $[Fe(NCS)_6]^{3-}$ etc.

10.16.2. Complexometric Titration: *Complexometric titrations (also called chelatometric titrations or chelometric titrations) are those titrations in which a metal ion is determined titrimetrically by way of complex formation with a strong multidentate chelating ligand.*

In complexometric titrations an organic dye is used as a metal indicator such that the metal-dye complex has a colour different from the colour of the free dye,

As the complexometric ligand reacts with the last small amount of the metal-dye complex it displaces the bound dye ligand from the metal-dye complex and the end point is marked by a change from the colour of the metal-dye complex to that of the metal indicator.

Stability Constant of the Metal Complex: Complexometric titration is made possible because of the fact that a metal complex of a multidentate ligand is extremely stable to dissociation i.e. it has a high stability constant. A chelating ligand imparts extra stability to a complex due to chelate effect. The greater the number of points of attachments of a ligand the greater will be its chelate effect. Ethylene-diamine tetraacetic acid (EDTAH$_4$ or H$_4$Y) (Table 10.1) and other amino poly-carboxylic acids are extremely suitable as complexometric ligands because these ligands can offer six points of attachments to a metal ion at a time in a single step. If we were to use ethylenediamine as a complexometric ligand the six coordination points of a metal ion would have been satisfied in three steps so that the resulting complex would have a far greater scope of dissociation. A comparison of the stability constants of metal—EDTA and metal-en complexes is thus instructive (Table 10.7). In some complexes eg: Cu^{2+}/Ni^{2+} complexes log K values of the EDTA complexes are close to the overall log K values of the en complexes but we have to remember that the latter complexes are not generated in a single step. Thus the basic requirements of a complexometric titration are that the metal and the complexometric ligand must react in a single step to satisfy all the coordination points of the metal ion and that the reaction must be fast enough to make a titrimetric estimation feasible.

$$H_4Y \rightleftharpoons H_2Y^{2-} + 2H^+; M^{2+} + H_2Y^{2-} \rightleftharpoons MY^{2-} + 2H^+$$
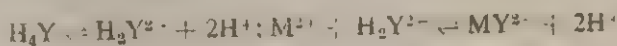
$$M^{n+} + Y^{4-} \rightleftharpoons MY^{(n-4)+} ; K = \frac{[MY^{(n-4)+}]}{[M^{n+}] [Y^{4-}]}$$

Metal (Metallochromic) Indicators: Metal indicators are organic dye ligands which help in ascertaining the end point of a complexometric tiration by changing colour from that of the metal-dye complex to that of the free dye. The metal-indicator ligand must form a suitably coloured complex at the same pH where the metal ion also prefers to complex with the chelometric ligand. Taking the example of Eriochrome Black T (10—XXVI) (H$_2$D$^-$) the following equilibria are known to occur:

$$H_2D^- \underset{5.3\text{-}7.3}{\overset{pH}{\rightleftharpoons}} HD^{2-} \underset{10.5\text{-}12.5}{\overset{pH}{\rightleftharpoons}} D^3$$

red   blue   orange yellow

The dye is written as H$_2$D$^-$ because the sulphonic acid proton is readily dissociated. Many metal ions eg: Ca^{2+}, Mg^{2+} react with this dye in NH$_4$Cl–NH$_4$OH buffer (pH ~ 11) to form red or purple red 1 : 1 metal-dye complex. The colour is very intense, as low as ~ $10^{-6}M$ Mg^{2+}/Ca^{2+} solution giving distinct colouration.

$$M^{2+} + D^{3-} \rightleftharpoons MD^- ; K = \frac{[MD^-]}{[M^{2+}] [D^{3-}]}$$

This metal-dye complex will react with EDTA as:

$$MD^- + Y^{4-} \rightarrow MY^{2-} + D^{3-}$$
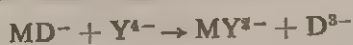
The requirements of a good metal-indicator are the following: (1) It must form with the metal ion a complex of reasonable stability, else the colour development will be poor due to dissociation. But the stability of the metal indicator complex has to be low compared to that of metal-EDTA complex. (2) The colour reaction should be specific or at least selective. (3) There should be a good contrast between the colour of the free indicator and the metal-indicator complex. (4) The indicator should meet these requirements at the pH of the complexometric titration.

Types of Complexometric Titrations: (1) *Direct titrations* are suitable for those metal ions whose reactions with the complexometric ligands are fast enough and for which good metal-indicators are available. Mg^{2+}, Ca^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+} belong to this class. (2) *Back titrations* are applied to those metal ions which react with complexometric ligands rather slowly. Chromium (III) is an example of this class. Excess standard EDTA is added to a chromium (III) solution, the solution boiled for sometime and the excess EDTA back titrated with a standard Mg^{2+} solution. Back titration is also preferred when there is no suitable indicator for the metal ion to be titrated.

(3) *Substitution titrations* are employed for those metals which do not give a reasonable colour with an indicator at the finish of the titration. In such a case either (*a*) a metal-EDTA complex which is weaker than the EDTA complex of the metal to be determined is used or (*b*) a suitable metal complex such as $[Ni(CN)_4]^{2-}$ is employed which reacts with the metal ion to be determined. In case (*a*) Mg-EDTA is generally employed:

$$Me^{2+} + MgY^{2-} \rightleftharpoons MeY^{2-} + Mg^{2+}$$
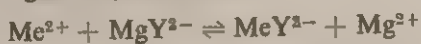
The equivalent amount of Mg^{2+} is then titrated with standard EDTA. For case (*b*) titrimetric determination of silver (I) forms an example:

$$[Ni(CN)_4]^{2-} + 2Ag^+ \rightleftharpoons 2[Ag(CN)_2]^- + Ni^{2+}$$
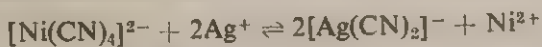
The liberated Ni^{2+} is then estimated with EDTA.

(4) *Indirect Titrations* are employed for estimations of anions. Phosphate may be precipitated as $MgNH_4PO_4$. This precipitate is collected, dissolved in acid, measured excess of standard EDTA added and pH adjusted to ~ 11. The excess EDTA is then titrated with a standard Mg^{2+} solution using Eriochrome Black T. Similarly sulphate is precipitated as $BaSO_4$, which is dissolved in excess EDTA and the excess EDTA is back titrated with standard Mg^{2+}.

Some Typical Complexometric Estimations: Disodium dihydrogen ethylene-diamine tetraacetate $Na_2H_2Y.2H_2O$ is a primary standard. The reagent is dried at $\sim 90°C$ where its dihydrate character is retained. A $0.1M$ solution contains 37.225 gm of the dihydrate per litre. EDTA solution should not be stored in glass equipment for prolonged period as it attacks soft glass dissolving out considerable amounts of cations present in soft glass. Polythene bottles are suitable for storing purpose.

1. *Total hardness of water:* Total hardness is due to dissolved calcium and magnesium salts. To 50 ml of such water is added 1 ml NH_4Cl-NH_4OH buffer of pH 11 followed by 4-5 drops of Eriochrome Black T (0.4% solution in methanol). The hard water is now titrated with 0.01 M standard EDTA till the colour changes from purple red to blue. Total hardness is expressed in parts of $CaCO_3$ per million of water:

$$1 \text{ ml of } 0.01M \text{ EDTA } = 1.000 \text{ mg of } CaCO_3.$$

2. *Determination of Calcium and Magnesium in a mixture:* In an aliquot the total magnesium and calcium are determined by EDTA titration using Eriochrome Black T as indicator. In another aliquot enough diethylamine base is added to precipitate magnesium quantitatively as $Mg(OH)_2$ and then 5 drops of *calcon* indicator (10-XXVIII) are added. The solution is titrated with EDTA till the colour changes from pink to blue.

Calcon, sodium 1-(2-hydroxy 1-naphthylazo)-2-naphthol-4 sulphonate, has a wider pH range of colour change:

$$H_2D^- \underset{7\text{-}8}{\overset{pH}{\rightleftharpoons}} HD^{2-} \underset{13\text{-}13.5}{\overset{pH}{\rightleftharpoons}} D^{3-}$$

pink   blue   pink

Calcon thus maintains its blue 'un-metallised' colour to ~ pH 13 which is in contrast to pH 11 offered by Eriochrome Black T. Thus magnesium can be thrown out of solution by raising the pH, and then calcium alone can be determined complexometrically.

(10-XXVIII)
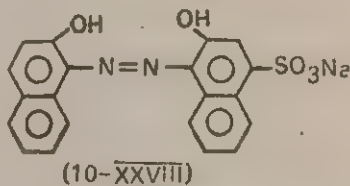
Calcon or Solochrome Dark Blue (sodium 1-(2-hydroxy-1-naphthyl azo)-2 naphthol-4-sulphonate

10.17. THE USES OF COORDINATION COMPLEXES IN INDUSTRY AND MEDICINE

(a) *Electroplating:* In order to achieve a fine grain deposit the concentration of the free metal ion in the electrolytic bath should be reduced to a small extent. For the electrodeposition of copper, silver, cadmium potassium cyanide is used as the complexing agent in the bath. The cyano complexes are little dissociated so that a fine grain deposit is obtained at the cathode.

(b) *Water Treatment:* Hard water does a lot of harm in industrial boilers and other equipments. EDTA addition is a very effective means of removing scale formation in boilers etc.

(c) Metallic nickel readily reacts with CO at about 50°C to form the complex $[Ni(\leftarrow CO)_4]$. This volatile complex readily decomposes around 200°C to give a very pure variety of nickel. This method is made use of in obtaining nickel free from traces of cobalt.

Medicinal Use: (*a*) In acute cases of lead poisoning intravenous injection of $CaNa_2$ EDTA is given to the patient. This results in rapid excretion of lead—EDTA complex in the urine. Since EDTA is not readily metabolised most of the calcium—EDTA appears also in the urine. (*b*) Wilson's disease is a disorder of the liver which leads to malfunctioning of the central nervous system. This disease is due to a deficiency of copper protein in the liver. Free copper ion accumulates in the liver due to a lack of copper specific ceruloplasmin. The excess and undesirable copper (II) is removed by administering the complexing ligand penicillamine Copper (II) forms a soluble complex via coordination with sulphur, nitrogen and oxygen donors of penicillamine.
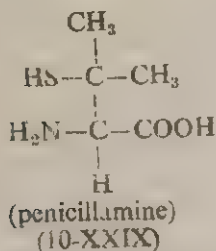
$$CH_3$$
$$|$$
$$HS-C-CH_3$$
$$|$$
$$H_2N-C-COOH$$
$$|$$
$$H$$

(penicillamine)
(10-XXIX)

10.18. DETECTION AND STRUCTURE DETERMINATION OF COMPLEXES

Had Werner been living he would have surely envied today's coordination chemists. The great Werner had merely two tools, conductivity and optical rotation and of course his own genius to help him see the light in the bewilderingly complex world of coordination compounds. Today's coordination chemists fortunately can cast their nets far and wide to detect and determine the structure of complexes. Some of these methods involve very complicated theory and complex experimental techniques. Some of the simpler methods are now pointed out.

1. *Solubility:* Complex formation is often indicated by abnormal solubility behaviour. For example, addition of 8-hydroxyquinoline (oxinH) to aluminium ion produces an insoluble precipitate of $[Al(oxin)_3]$ or addition of ammonia to insoluble silver chloride provides very soluble $[Ag(NH_3)_2]^+$.

2. *Colour:* Transition metal complexes involve a change in *d*-orbital ordering. Low energy transitions from t_{2g} to e_g (for octahedral complexes) or from *e* to *t* (tetrahedral complexes) occur in such complexes. These transitions develop typical colours, the absorptions being in the visible range of the spectrum. A colour change is generally an indication of complexation. For example, addition of ammonia to tetraaquo copper (II) ion leads to an intense blue colour due to the formation of $[Cu(NH_3)_4]^{2+}$. Replacement of weaker donor H_2O by a stronger donor NH_3 shifts the absorption band to higher energy (lower wave length) from ~ 8000 A to ~ 6000 A. A detailed study of the optical spectrum often fixes the stereochemistry exactly (Chapter 11).

3. *Magnetic Susceptibility:* A measurement of the magnetic susceptibility sometimes indicates the formation of a complex alongwith the nature of the bonding and stereochemistry. For example, bis (dimethylglyoximato) nickel (II) and bis (biguanide) nickel (II) are both diamagnetic indicating a four coordinate square planar structure whereas $M_2[NiCl_4]$ complex is paramagnetic (~ 3.9 B.M.) exhibiting a tetrahedral structure.

4. *Conductance measurements:* Conductivity of $[Co(NO_2)_2(en)_2]X$ is that of a uni-univalent electrolyte. This means that the two univalent, monodentate nitro groups are inside the complex zone. The presence of X^- as an anion can be easily detected by suitable chemical tests. Non-electrolytic behaviour of $[Pt(NH_3)_2 Cl_2]$ shows the two chloride ions are also bound to platinum.

5. *pH measurements:* Salicylic acid is a weak acid but in presence of a complexing metal ion enough H^+ ions will be released in solution to make the solution substantially acidic. Quantitative measurements of such H^+ ion liberation, in fact, provide an evaluation of the stability constant of the metal complexes.

There are many other techniques such as dipole moment measurements (Chapter 5), infrared spectra, nuclear magnetic resonance, electron spin resonance etc. which also may furnish valuable informations on the structure of the complex. We prefer for obvious reasons not to discuss these techniques in this text.

10.19. METAL COMPLEXES IN LIVING SYSTEMS

Metal chelates play vital role in living systems. The green colouring matter of plants, called chlorophyll, is a planar complex of Mg^{2+} with four nitrogen sitting at the four corners of a square plane (10-XXX). The N_4 unit forms a part
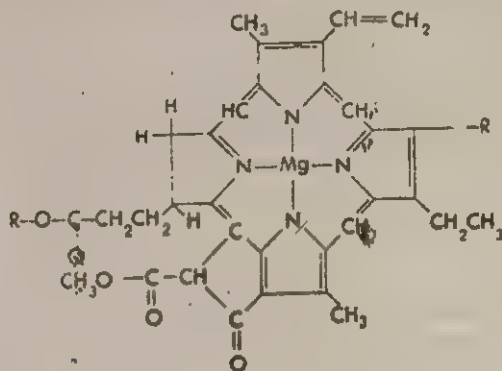
10-XXX. Structure of chlorophyll

of 16-membered natural macrocycle. Chlorophyll serves as a catalyst in the photosynthetic conversion of CO_2 to carbohydrates within the cells of green plants. Chlorophyll is instrumental in the syntheses of glucose from CO_2 and H_2O by the green plant via a series of very complicated reactions. Chlorophyll absorbs red light (of about 700 nm). This excites the molecule for a series of redox reactions. A very crude description is that H_2O is split up into a very reducing form of hydrogen. This reacts with atmospheric CO_2 and produces glucose and water:

$$2H_2O \rightarrow 2H_2 \text{ (highly reducing)} + O_2$$

$$6CO_2 + 6H_2 \rightarrow C_6H_{12}O_6 + 3O_2$$
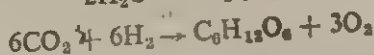
Hemoglobin, the pigment that imparts red colour to the human blood, is porphyrin complex of ferrous iron (10-XXXI) being coordinated to four nitrogen

17

atoms and additionally coordinated to a water molecule. The water molecule appears to be replaceable *reversibly* by a molecule of oxygen to give oxyhemoglobin:

$$\text{Hemoglobin} + O_2 \rightleftharpoons \text{Oxyhemoglobin} + H_2O \cdot$$
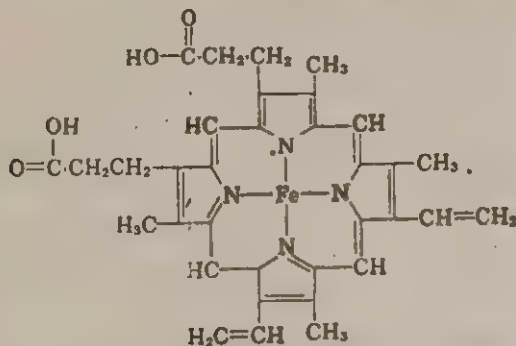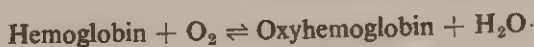
10-XXXI Heme: iron porphyrin complex

This equilibrium can be shifted either way by a change of pressure of oxygen. In human lungs blood is saturated with air and the hemoglobin is completely changed to the oxyhemoglobin form. As the blood runs through the arteries to the tissues the oxygen pressure dwindles and the bound oxygen liberated. This free oxygen is used in the combustion of food. By this reversible process hemoglobin serves as an oxygen carrier. It is of vital importance to know that strong field ligands like CO or CN^- can readily displace oxygen from oxyhemoglobin. This leads to stoppage of flow of oxygen to the tissues—ultimately causing paralysis or even death.

STUDY QUESTIONS

1. Which of the following ions or compounds can serve as ligands in complexes? Which ones can serve as monodentate, bidentate or as monodentate and bidenatate both? $(C_6H_5))_3P$, $(C_6H_5)_3PO$, Cl^-, $(C_6H_5)_2P-CH_2-CH_2-P(C_6H_5)_2$, BF_3, $F_3B.NH_3$.
   Can any of these function as bridging ligands?

2. How would you proceed to establish the formulations given to the following compounds? $[Co(NH_3)_6] \, Cl_3$, $[Pt \, Cl_2(NH_3)_2]$, $[Pt(NH_3)_4] [PtCl_4]$, $[Co(en)_2(acac)]Cl$.

3. Assuming monomeric and also dimeric formulations what different types of isomerism are possible in the following cases:

$[Pt(NH_3)_2Cl_2]$; $[Pt(NH_2-CH_2-COO)_2]$; $[Pt(NH_2-CH_2-CH_2-NH_2)(NH_2-CH_2-COO)]^+$; $[Co(NH_3)_5 \, (NO_2)] (NO_3)_2$.
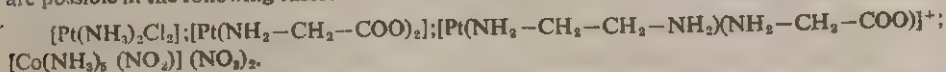
4. Can $[Co(NH_2-CH_2-COO)_3]$ exist in enantiomeric forms? If so, can you apply the diastereoisomeric method for the separation of the enantiomers?

5. Normally asymmetry should not appear in a tetrahedral complex unless all four groups are different. But bis (salicylaldehydato) boron, a tetrahedral complex shows optical activity. Comment. What will happen if we replace salicylaldehydato group by a catecholato group?

6. You are supplied with a sufficient amount of a sample said to be $[Co(NO_2)_2(en)_2]Cl$. What experiments would you like to perform to establish completely its identity?

7. Examine with the help of the shapes of d-orbitals the relative ordering of the orbitals on making a tetragonal distortion of an octahedral complex ultimately leading to a square planar complex.

8. List the isomers which may exist for the following: $[Co(en)_2 (NH_3)Cl]^{2+}$; $[Cr(NCS)_6]^{3-}$; $[Ni(en)_3]^{3+}$.

9. (a) Write the systematic names for the following:

$[Cr(NH_3)_4Cl_2]Cl$; $[Pt(NH_3)_4en]^{4+}$ $[Co(ox)_3]^{3-}$; $K[Co(EDTA)]$
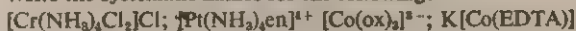
(b) Give the valence bond and crystal field descriptions of $[Cu(NH_3)_4]^{2+}$, $[Fe(CN)_6]^{3-}$, $[FeCl_4]^-$ and $[Co(NH_3)_6]^{3+}$.

10. Guess the probable explanation for the formulas of two common sulphates of copper (II) and nickel (II) being $CuSO_4. 5H_2O$ and $NiSO_4, 7H_2O$.

11. Why is the colour of $[Cu(NH_3)_6]^{2+}$ different from that of $[Cu(H_2O)_6]^{2+}$?

12. Isomerism of hexahydrated chromic chloride depends on the difference in the mode of linking of the molecules of water. Do you agree entirely?

13. Define and give examples of (a) complex ion (b) central atom (c) ligand (d) coordination number (e) coordination sphere.

14. Define a metal chelate complex. Discuss some applications of metal chelates. How would you classify chelate complexes?

15. A polydentate ligand may not use all its donor centres for complexation. Comment.

16. Sketch a few common techniques of detecting formation of complex species.

17. How would you proceed to distinguish between cis and $trans$ isomers of a complex?

18. $K_2[NiF_6]$ is diamagnetic while $K_3[CoF_6]$ is paramagnetic. Both nickel (IV) and cobalt (III) are d^6 systems. How would you explain the difference in magnetic behaviour?

19. Discuss the origin of colour in metal complexes.

20. Discuss the usefulness of CFSE in explaining many behaviours of transition metal complexes.

21. Give a concise account of complexometric titration. Explain in this context why ethylene-diamine cannot serve as a complexometric titrant although it is a strong field ligand.

22. Present a concise account of Jahn Teller effect in transition metal complexes in octahedral and tetrahedral geometries. Can similar effect occur in filled d^{10} complexes?

23. "Splitting of the d orbitals is dependent on the stereochemistry of the complex."—Discuss.

24. Explain why Ti^{3+} form coloured aqueous solution while Ti^{4+} gives colourless solution.

25. What is formation constant? On what factors does it depend?

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Magnetochemistry

Behaviour of inorganic chemicals in an applied magnetic field has provided important clues to our understanding of the nature of bonding, valence and stereochemistry of such substances. Whereas the details and finer aspects of this branch are very complex, only a broad outline of the background principles can be attempted here.

11.1. DEFINITIONS

Pole Strength: A unit pole is defined as a pole which when placed in vacuo one cm. away from another unit pole repels or attracts it with a force of one dyne.

Intensity of a Magnetic Field ; A magnetic field is said to have unit intensity at a point if it exerts a force of one dyne on a unit pole placed at that point. Intensity is also expressed in terms of the number of lines of force per square cm. Therefore a magnetic field has a unit intensity if one unit line of force passes through 1 sq. cm.

Intensity of magnetisation: This is defined as the pole strength induced per unit area. Taking m as the pole strength induced over an area A and l as the length of a magnetic dipole:

$$I = \frac{m}{A} = \frac{m.l}{A.l} = \frac{\text{magnetic moment}}{\text{volume}}$$

Gauss's Law and Magnetic Induction: Consider a unit pole at the centre of a sphere of 1 cm radius (surface area $= 4\pi$ sq. cm). By definition it will act upon another unit pole anywhere on the surface of the sphere with a force of 1 dyne i.e. will generate a unit magnetic field all over the surface. Since a magnetic field of unit intensity gives unit line of force per sq. cm. it follows that 4π lines of force will emanate from a unit pole. Gauss's law states that the magnetic induction over a closed surface is 4π times the pole enclosed. The total magnetic induction, B, is:

$$B = H + 4\pi \times \text{pole strength per unit area}$$
$$= H + 4\pi I \text{ where } H = \text{strength of the applied field. } B \text{ represents the}$$

total number of lines of force across a unit surface of the material which has been subjected to H lines of force due to the imposed field.

Magnetic Permeability, P, is given by:

$$P = \frac{B}{H} = 1 \times 4\pi \frac{I}{H} = 1 \cdot 4\pi\kappa$$

where κ is called the magnetic susceptibility per unit volume. Intensity of magnetisation induced in a substance is proportional to the strength of the applied field H. $I \propto H$; $I = \kappa H$; $\therefore \kappa = I/H$ so that κ may also be viewed as a proportionality constant. Thus κ tells us how susceptible a substance is to induced magnetisation. When $\kappa = 0$, P becomes equal to 1. P and κ may be considered dimensionless. P is the ratio of the density of lines of force within the body to the density of lines of force in a vacuum.

Gram Susceptibility, χ_g, is equal to κ/ρ where ρ is the density.

The molar susceptibility is given by $\chi_M = \chi_g \times M$, where M is the molecular weight of the substance. .

Magnetic Moment: When a field H acts on a magnetic dipole N—S of length I and pole strength m, its N and S poles will experience a force of $+ mH$ and $- mH$ (Fig. 11.1). These two equal but opposite forces constitute a couple, the turning moment of which is given by the product of force and distance. Turning moment $= mH \times PN = mH$ I sin $\theta = mlH$ sin $\theta = \mu H$ sin θ. The quantity $\mu = ml$ defines the magnetic moment and serves as a measure of the turning effect. This is by far the most important quantity used in magnetochemistry. The magnetic susceptibility (χ_M) of a sample is experimentally determined and is converted to the magnetic moment. The determined moment is then compared with the theoretically predicted moment values and important conclusions are drawn with regard to valence, structure and bonding of the central metal ion in a compound.
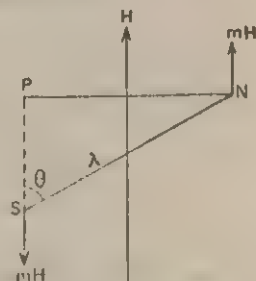
FIG. 11.1. Forces on a magnetic dipole showing the moment or turning effect.

11.2. CLASSIFICATION OF MAGNETIC SUBSTANCES

When κ or χ is negative, permeability of a body is less than unity. A reduction of lines of force of the applied field H occurs inside such a body and it moves to regions of lowest field strength. Such a body is called diamagnetic (Fig. 11.2). When κ or χ is positive permeability is greater than unity. The lines of force of the applied field H tend to concentrate inside the substance and the substance tends to move into regions of highest field strength. Such a body is called paramagnetic. When κ or χ is zero, permeability is unity and the lines of force pass through a vacuum.

Ferromagnetic substances have their permeability very much greater than

unity. Antiferromagnetics have their χ values much lower than those of the usual paramagnetics.
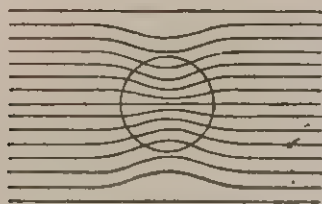
FIG. 11.2. Diamagnetic substance in a magnetic field
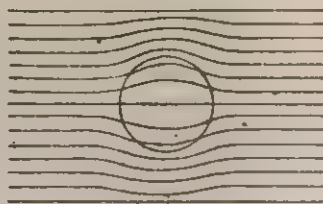
FIG. 11.3. Paramagnetic substance in a magnetic field

A magnetically dilute substance is one wherein the individual paramagnetic centres in crystal lattice are sufficiently apart to minimise any further magnetic interaction between near neighbours. Conversely, substances where the individual magnetic centres in the crystal lattice are close enough to initiate further magnetic interaction are magnetically concentrated. [Ni $(H_2O)_6$] Cl_2 is an example of a magnetically dilute system while cupric acetate, in reality $Cu_2(CH_3COO)_4.2H_2O$ (29-III), is magnetically concentrated. The unpaired electrons of the two copper atoms are known to interact with each other.
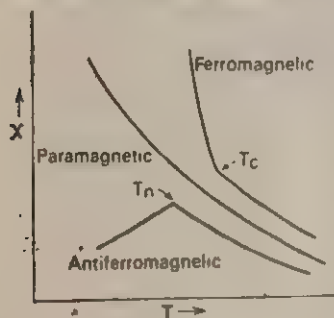
FIG. 11.4. Variation of χ_g with temperature (a) ferromagnetic (b) normal paramagnetic (c) antiferromagnetic. T_C and T_N indicate the Curie temperature and the Neel temperature.

Table 11.1. provides a classification of the more important types of magnetic substances along with their characteristic features. The variation of χ_g with temperature for different magnetic bodies is shown in Fig. 11.4.

11.3. ORIGIN OF MAGNETIC PROPERTIES

Electrons are responsible for the magnetic behaviour of chemical substances. Adopting the classical particle picture of an atom, an electron is assumed to move around the nucleus in an orbit. The electron also spins around its own axis. The first of these motions is comparable to the movement of electric current in a loop of wire, and this orbital motion therefore produces a magnetic field. The spinning motion also produces a magnetic effect. These magnetic effects can be expressed in terms of magnetic moments arising as if out of some small micromagnets placed at the centre of the atom.

Table 11.1. Classification and Characteristics of Magnetic Bodies

Type	Caused by	Magnitude of χ_g	Temperature & Field dependence of χ_g	Example
Diamagnetic	Orbital motion of electrons. Best perceptible when the body has all its electrons paired i.e. when there is no permanent spin moment.	small and negative $\sim -1 \times 10^{-6}$ cgs units	Temperature independent and field independent	H_2, KCl, organic ligands
Paramagnetic	Electrons with unpaired spin i.e. with resultant angular momentum	Small and positive $\sim +10$ to $10^3 \times 10^{-6}$ cgs units	Varies inversely with temperature. Field independent	$[Ni(H_2O)_6]Cl_2$ $[CoCl_4]^{2-}$
Ferromagnetic	Lattice of particles with electrons having parallel spin	Very large and positive 10^{-2} to 10^4 cgs units	Complicated: above a particular temperature called Curie temperature, it behaves as a paramagnet. Below this temperature χ_g rapidly increases.	Metallic iron
Antiferromagnetic	Two lattices of particles having spins of one lattice anti parallel to the spins of the other lattice	Positive and very small ~ 0.1 to $10^2 \times 10^{-6}$ cgs units	Above a particular temperature called Neel temperature the substance behaves as paramagnetic but below the Neel temperature susceptibility continues to drop with decrease in temperature	$KNiF_3$; many dimeric complexes of copper (II) and oxovanadium (IV)

11.4. SINGLE ELECTRON SYSTEM : ORBITAL MAGNETIC MOMENT

An electron of charge e and mass m moving in an orbit with an average angular velocity $\bar{\omega}$ makes $\omega/2\pi$ revolutions per second (Fig. 11.5). The strength of the current carried is given by $e\bar{\omega}/2\pi$ esu or $e\bar{\omega}/2\pi c$ emu where c is the velocity of light. According to Ampere's theorem the magnetic moment, μ_l, of a current in a loop is given by the product of the current and the area of the loop.

μ_l = magnetic moment due to the current

= current strength × area of the orbit
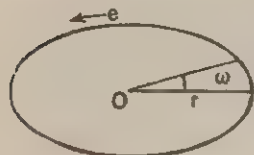
Fig. 11.5. Orbit of an electron

$$= \frac{e\bar{\omega}}{2\pi c} \times \mu \bar{r}^2 = \frac{e\bar{\omega}\bar{r}^2}{2c} \text{ where } \bar{r}^2 \text{ is the mean square}$$

...dius of the electron orbit. This orbital magnetic moment can be conceived of as the moment of a micromagnet placed at the origin 'O' at right angles to the plane of the orbit.

The above relation becomes more meaningful when correlated with angular momentum of the electron. Angular momentum of the electron about 'O' is given by mvr. But v being equal to $\bar{\omega}r$ we have (taking the mean square radius):

angular momentum $= m\bar{\omega}\bar{r}^2$.

Quantum mechanics shows that angular momentum of an electron is given by $\sqrt{l(l+1)}\, h/2\pi$ where l is the orbital (azimuthal) angular momentum quantum number. Thus

$$m\bar{\omega}\bar{r}^2 = \sqrt{l(l+1)}\frac{h}{2\pi} \qquad \therefore \bar{\omega}\bar{r}^2 = \sqrt{l(l+1)}\frac{h}{2\pi m}$$

$$\therefore \mu_l = \frac{e\bar{\omega}\bar{r}^2}{2c} = \sqrt{l(l+1)}\frac{eh}{4\pi mc} = \sqrt{l(l+1)}\,\beta$$

where β is the Bohr magneton, 0.927×10^{-20} ergs /gauss.

11.5. SINGLE ELECTRON SYSTEM : SPIN MAGNETIC MOMENT

The ratio of orbital magnetic moment ($e\bar{\omega}r^2/2c$) to the orbital angular momentum ($m\bar{\omega}r^2$) is $e/2mc$. The ratio of the spin magnetic moment to the spin angular momentum is, due to the anomalous behaviour of spin, e/mc.

This is twice the ratio ($e/2mc$) for orbital motion. Recall that the spin angular momentum of an electron is given by $\sqrt{s(s+1)}\frac{h}{2\pi}$ (Chapter 1). Then we have:

Spin magnetic moment $= (e/mc) \times$ spin angular momentum

$$\therefore \mu_s = \sqrt{s(s+1)}\frac{eh}{2\pi mc} = 2\sqrt{s(s+1)}\frac{eh}{4\pi mc} = 2\sqrt{s(s+1)}\,\beta$$

The above results can be rewritten in the following forms: $\mu_l = g\sqrt{l(l+1)}\beta$ and $\mu_s = g\sqrt{s(s+1)}\,\beta$ where $g = 1$ for orbital moment and $g = 2$ for spin

moment. The 'g' is called the gyromagnetic ratio and is the ratio of the appropriate magnetic moment to the appropriate angular momentum.

11.6. DIAMAGNETISM AND PASCAL'S CONSTANTS

Orbital motion of the electron introduces a magnetic field perpendicular to the plane of the orbit. On the application of an external magnetic field H the nature of the electron orbits, their tilts to the applied field and the movement of the electrons in the orbits are not altered but the orbits continue to rotate around the axis of the applied field maintaining the same tilt. *The applied field thus introduces an extra rotation of the charge, which may be viewed as an additional orbital motion.* In effect the orbit normal describes a cone (Fig. 11.6) about the direction of H.

This induced motion is called a precessional motion (Fig. 11.6). Larmor has shown that this precessional motion has a velocity $\frac{eH}{2mc}$. It is at once apparent that such pre-cessional motion will cease to occur in the absence of H. This motion will generate a magnetic field in opposition to the applied field H and in addition to the possible orbital and spin effects of the electron. Thus, the diamagnetic moment becomes:

FIG. 11.6. Precession of an electron orbit about the direction of H.

$$\Delta \mu = -\frac{e \text{ (precessional angular velocity) (precessional radius)}^2}{2c}$$

$$= -\frac{e.eH.\overline{r_1^2}}{2c.2mc} = -\frac{e^2 H \overline{r_1^2}}{4mc^2}$$

where $\overline{r_1^2}$ is the mean square radius of the precessional orbit perpendicular to the direction of H. If the electron has the coordinates x, y, z, then $\overline{r^2} = \overline{x^2 + y^2 + z^2}$. Taking the xy plane, that is the plane obtained by the projection of the orbit perpendicular to the direction of H, z can be neglected, so that:

$$\overline{r_1^2} = \overline{x^2 + y^2} = \tfrac{2}{3}\overline{r^2}$$

Similar mean square radius value will be obtained for other possible orientations.

$$\Delta \mu = -\frac{e^2 H}{4mc^2} \cdot \tfrac{2}{3} \overline{r^2} = -\frac{e^2 H}{6mc^2} \overline{r^2}$$

In the case of a multielectron atom $\overline{r^2}$ is replaced by $\Sigma \overline{r^2}$

For a gram atom, $\Delta \mu_A = -N \frac{e^2 H}{6mc^2} \Sigma \overline{r^2}$ (N is Avogadro number)

Now recall $I = \frac{\text{magnetic moment}}{\text{volume}} = \frac{\Delta \mu_A}{V}$ (V = molar volume)

$$\text{Again } \chi_M = \chi_g \times M = \frac{\chi_v}{\rho} \times M = \frac{I}{H} \times \frac{M}{\rho} = \frac{J}{H} \times V$$

$$= \frac{\Lambda \mu_A}{V \times H} \times V = \frac{\Delta \mu_A}{H} = -N \frac{e^2}{6mc^2} \Sigma r^2$$

$$\simeq -2.83 \times 10^{10} \Sigma r^2$$

The following points are to be noted:

1. The negative sign indicates that diamagnetism is an induced phenomenon and acts in opposition to the applied field.
2. It is an inherent, universal property of all chemical substances.
3. Diamagnetism is independent of temperature and field strength. H and T do not appear in the susceptibility equation.
4. The radii of the electron orbits decide the magnitude so that the larger the orbit size the bigger the diamagnetism.

Pascal derived from measurements of diamagnetic susceptibilities of a very large number of organic substances the following empirical equation:

$$\chi_M \text{ (dia)} = \Sigma n_A \chi_A \text{ (dia)} + \Sigma \lambda$$

where n_A is the number of A atoms of gram atomic susceptibility χ_A that constitute the molecule. λ is a constitutive correction that empirically takes into account the nature of the bonds and atoms present in the molecule. χ_A and λ are called Pascal's constants.

Pascal could sense that diamagnetism possibly originates from two sources: one being the atoms of the elements (giving χ_A) and the other being the type of bonding between the atoms (giving λ). He also realised that different constitutional corrections for different types of bonding were to be used. The evaluation of r^2 in a compound is insuperable. Pascal has solved the problem by giving it an empirical bias. Consider the following experimental data of Pascal :

ethyl acetate. $CH_3COOC_2H_5$	$\chi_{dia} = -57.5 \times 10^{-6}$	$\Big\} -17.8$
ethyl chloroacetate, $CH_2ClCOOC_2H_5$	$= -75.3$	
acetone, CH_3COCH_3	$= -35.1$	$\Big\} -17.9$
chloroacetone, $CH_2ClCOCH_3$	$= -53.0$	
benzene, C_6H_6	$= -57.4$	$\Big\} -3 \times 17.8$
trichlorobenzene, $C_6H_3Cl_3$	$= -110.9$	

The mean difference, -17.85×10^{-6}, represents the difference arising as a result of substitution of one H by a Cl. Taking χ_A of chlorine as -20.95×10^{-6} Pascal obtained χ_A of hydrogen as -3.1×10^{-6}. Pascal's original values have undergone slight correction due to revision of the susceptibility datum of his calibrant water. Using Pascal's constants the diamagnetic susceptibility of acetylacetone is calculated as -50.8×10^{-6} cgs units while the experimental value is -52.0×10^{-6}.

In order to compute the susceptibility (and also the moment) of a paramagnetic substance, the diamagnetic effect of the associated groups or ions is to

be added as a correction. Pascal's constants are of invaluable aid in making such correction, an independent measurement on the groups or ions being unnecessary. In the field of coordination complexes, often syntheses of otherwise untractable ligands are realised in the form of transition metal complexes only. In such cases, diamagnetic correction cannot be made by actual measurements on the ligands, and Pascal's constants are the only solutions to the problem.

11.7. MULTIELECTRON SYSTEMS

11.7.1. Coupling Schemes and Ground Terms : It has been noted in single electron system that paramagnetism arises out of orbital and/or spin angular momenta. In multielectron system it is therefore imperative that one knows the resultant angular momenta of the system.

The orbital angular quantum number, l, can take up any integral value from 0 to $(n-1)$ where n is the principal quantum number. A particular value of l is associated with an orbital angular momentum vector, l, such that $l = \sqrt{l(l+1)} \frac{h}{2\pi}$ This vector can assume $2l + 1$ orientations in space. If a particular direction is specified, for instance the direction of an applied magnetic field, the projections of l in the direction of the field may have values $+l$ to $-l$. These projection values are the magnetic quantum numbers m_l.

Similarly the spin quantum number, s, is associated with a vector s, where $s = \sqrt{s(s+1)} \frac{h}{2\pi}$. The value of s is always $\frac{1}{2}$ and single electron m_s values will be either $+\frac{1}{2}$ or $-\frac{1}{2}$ being parallel or antiparallel to the applied magnetic field.

Orbital angular momentum vectors, l of individual electrons can couple to give a resultant vector L. The angular momentum vector of an electron is perpendicular to the plane of rotation of the electron and the direction follows from a right handed screw motion (Chapter 1). Electrons have their planes of motion inclined to each other. The vectors of the individual electrons precess about a common axis while maintaining their mutual inclination and thus giving the resultant vector L (Fig. 11.7). In order to keep electrostatic repulsions at a minimum electrons tend to stay on opposite sides of the nucleus and also tend to rotate about the nucleus in the same direction. This leads to a maximisation of the resultant L vector.

Similarly the individual spin vectors, s, of electrons can also couple to give rise to a resultant spin vector, S. These orbital and spin resultant vectors L and S can again couple (via the magnetic dipoles they induce) to give a resultant vector J. This L-S coupling is also know as Russell Saunders coupling :

$$(s_1, s_2 \ldots)\ (l_1, l_2 \ldots) = (S, L) = J$$

The strengths of the various couplings follow the order :

$$s_i\ s_k > l_i l_k > S, L$$

Another coupling scheme involves the coupling of the spin and orbital vectors of

individual electrons (**j** vectors), being followed by a coupling of the individual **j** vectors. This is called **j·j** coupling but this is of little importance for our purpose.

Each of these vectors has associated with it a quantum number. The resultant quantum numbers can have values varying by integral steps between the maximum and minimum resultants, and this will be true for both orbital and spin quantum numbers. Thus coupling of the orbital quantum numbers $l_1 = 1$ and $l_2 = 2$ of two electrons can give resultant values 3, 2 and 1, these being the values of L permitted to vary between $l_1 + l_2 = 3$ and $l_2 - l_1 = 1$. If two electrons have their spin quantum numbers as $\frac{1}{2}$ and $\frac{1}{2}$ then the resultant spin quantum number can assume values 0 or 1. A multielectron system is designated by certain symbols S, P, D, F, G, H, etc. standing for the multielectron L values of 0, 1, 2, 3, 4, 5, etc respectively. Such symbols carry a left hand superscript designating the spin multiplicity $2S + 1$ and a right hand subscript giving the J value.

FIG. 11.7. Coupling of *l* vectors

Spin multiplicity signifies the number of ways the spins (i.e. M_s) can be arranged. Thus a 2-electron system can be arranged in three ways to have $M_s = +1, 0, -1$. Note that the spin multiplicity is also $3 = (2(\frac{1}{2}+\frac{1}{2})+1)$. Thus the number of orientations of the spin vectors in a magnetic field is indicated by $2S + 1$. The multielectron L and multielectron S can couple to give further resultants, again varying in integral steps between $|L + S|$ and $|L - S|$. Thus $L = 3$ and $S = 1$ can couple to give J values 4, 3 and 2. A particular pair of L and S gives a term, that is, defines a particular energy state. The $^3F_2$ term indicates that this multielectron system has a spin multiplicity 3(= 2 unpaired electrons) and a multielectron L value 3. Furthermore of the possible J values (4, 3 and 2), the $^3F_2$ term is the one with $J = 2$. A multielectron system can give rise to a large number of terms. The following rules due to Hund help in deciding the lowest energy ground state of the multielectron system :

1. *The ground state will always have the highest value of the spin multiplicity.* This rule leads to minimisation of interelectronic repulsion. Electrons hate to share orbitals.

2. *When several terms with the same spin multiplicity are possible the one with the largest L value will be the ground state.* In order to minimise repulsive effects electrons tend to move *in the orbits in the same direction.* Vector addition of *l*'s therefore leads to maximisation of *L* (examine Fig. 11.7).

3. *For a half filled or less than half filled shell, the lowest J forms the ground state, and for a more than half filled shell, the highest J forms the ground state.* This rule follows from hole equivalency theorem to be discussed shortly.

Let us take an example, say a d^3 ion, to see how the ground state term is determined. Note first that the lower lying s and p orbitals of the ion are all filled. It is easily shown that all filled shells have zero orbital and spin momenta and hence no paramagnetic moments. A p level has $l = 1$, so that m_l can have values $+1, 0$ and -1. So, of the six p electrons, two have $m_l = +1$, two have $m_l = 0$ and two have $m_l = -1$. Thus we get $\Sigma m_l = M_L = 0$ which means that the resultant L is also zero.

Again, three electrons have $m_s = +\frac{1}{2}$ and the other three have $m_s = -\frac{1}{2}$ so that $M_s = 0$ which means S is also zero. Thus a filled shell or subshell carries no paramagnetism.

Allowing the highest spin multiplicity subject to Pauli principle, the three d electrons (with $l = 2$) can be arranged one each in the orbitals $m_l = 2, m_l = 1$ and $m_l = 0$ so as to get the highest $M_L = 3$, that is, the highest L value 3. Note other arrangements will give lower M_L and lower L. The ground state will have a maximum number of unpaired electrons, that is, a spin quantum number $\frac{3}{2}$ which means a spin multiplicity of 4. Therefore the ground state has $L = 3$ and $S = \frac{3}{2}$. J can have values $\frac{3}{2}, \frac{5}{2}, \frac{7}{2}$ and $\frac{9}{2}$. Since d^3 configuration is less than half filled the lowest $J = \frac{3}{2}$ will be the ground state and hence the full ground state symbol is $^4F_{3/2}$. Table 11.2 gives the ground state symbols of $3d^n$ configurations.

Table 11.2. Ground Terms for $3d^n$ Configurations

$3d^n$	$m_l =2$	1	0	-1	-2	M_L	M_s	Ground Term Symbol
$3d^1$	↑					2	$\frac{1}{2}$	$^2D_{3/2}$
$3d^2$	↑	↑				3	1	$^3F_2$
$3d^3$	↑	↑	↑			3	$\frac{3}{2}$	$^4F_{3/2}$
$3d^4$	↑	↑	↑	↑		2	2	$^5D_0$
$3d^5$	↑	↑	↑	↑	↑	0	$\frac{5}{2}$	$^6S_{5/2}$
$3d^6$	↑↓	↑	↑	↑	↑	2	2	$^5D_4$
$3d^7$	↑↓	↑↓	↑	↑	↑	3	$\frac{3}{2}$	$^4F_{9/2}$
$3d^8$	↑↓	↑↓	↑↓	↑	↑	3	1	$^3F_4$
$3d^9$	↑↓	↑↓	↑↓	↑↓	↑	2	$\frac{1}{2}$	$^2D_{5/2}$

11.7.2. Derivation of Russell Saunders Terms : We examine the case of carbon atom which has the ground state electronic configuration:

$$\underset{1s}{↑↓} \qquad \underset{2s}{↑↓} \qquad \underset{2p_x}{↑} \qquad \underset{2p_y}{↑} \qquad \underset{2p_z}{\_\_}$$

Since both the $1s$ and $2s$ levels are saturated their $L = 0$ and $S = 0$. So the case of carbon atom is one of a p^2 configuration. A p electron has $l = 1$ so that each of the two p electrons has m_l values $+1, 0, -1$. Each p electron has m_s value

of $+\frac{1}{2}$ or $-\frac{1}{2}$. We have now to consider all the possible combinations of m_s's and m_l's:

$$M_s = \Sigma m_s \text{ and } M_L = \Sigma m_l$$

A symbol 1^+ means we have an electron whose m_l is $+1$ and m_s is $+\frac{1}{2}$. Taking the m_l and m_s values of the first electron we can write the following six arrangements: 1^+, 1^-, 0^+, 0^-, -1^+ and -1^-. Similar six arrangements are possible for the second electron also. Of a total of $6 \times 6 = 36$ arrangements the six sets $(1^+, 1^+)$, $(1^-, 1^-)$, $(0^+, 0^+)$, $(0^-, 0^-)$, $(-1^+, -1^+)$, $(-1^-, -1^-)$ are not Pauli permitted. Of the remaining 30 half become physically redundant since sets $(1^+, 1^-)$ and $(1^-, 1^+)$ cannot be distinguished. Finally 15 distinct arrangements of m_l and m_s known as *microstates* remain (Table 11.3). Note bat the microstates in the column of $M_s = 1$ just change sign of their spins in the column of $M_s = -1$. $M_L = 2$ means that the multielectron L has to be 2. Had L been 3, M_L would

Table 11.3. Microstates for p^2 configuration:

M_s $\rightarrow$ M_l $\downarrow$	1	0	-1
2		$(1^+, 1^-)$	
1	$(1^+, 0^+)$	$(1^+, 0^-), (1^-, 0^+)$	$(1^-, 0^-)$
0	$(1^+, -1^+)$	$(1^+, -1^-), (1^-, -1^+)$ $(0^+, 0^-)$	$(1^-, -1^-)$
-1	$(-1^+, 0^+)$	$(-1^+, 0^-), (-1^-, 0^+)$	$(-1^-, 0^-)$
-2		$(-1^+, -1^-)$	

have varied from $+3$ to -3. When $L = 2$, M_L varies $+2$ to -2. With $M_L = 2$ in this p^2 case M_s value of the microstate is 0 so that $S = 0$ i.e. $2S + 1 = 1$. Therefore ^1D symbol will cover *five* microstates. It does not matter which five microstates we take so long as these microstates have $M_s = 0$ and $M_L = +2$, $+1, 0, -1$ and -2. Now take the case of $M_L = 1$ and $M_s = 1$ which orginates from $L = 1$ and $S = 1$ i.e. a ^3P term. $L = 1$ means $M_L = +1, 0, -1$ and $S = 1$ means $M_s = +1, 0, -1$. Therefore a total of *nine* microstates are covered by the ^3P term. After segregating these $5 + 9 = 14$ microstates in Table 11.3 we are left with only one having $M_L = 0$ and $M_s = 0$ i.e. ^1S term. Note that the 15 microstates are accounted for by the spin and orbital degeneracy:

^1D means $(2S + 1)(2L + 1)$ i.e. $1 \times 5 = 5$ microstates

^3P means $3 \times 3 = 9$,,

^1S means $1 \times 1 = 1$,,

Hund's rule predicts the following energy order: $^3P < {}^1D < {}^1S$.

11.7.3. Russell Saunders Terms and Hole Equivalence Theorem : Fig. 11.11 gives the Russell Saunders terms arising out of the d^n electronic configurations.

An interesting result is immediately evident that in each of the pairs (d^1, d^9), (d^2, d^8), (d^3, d^7) and $(d^4, a-)$ one configuration has the same terms as the other. This equivalence follows from the *hole equivalency theorem* (also known as *hole formalism*). A d^8 electron system may be conceived to have resulted from the introduction of two positorns in a filled d^{10} electron subshell. Since a filled d^{10} subshell can contribute only 0 to the M_s and M_L values the Russell Saunders terms due to d^{10} electron + d^2 positron will solely arise due to the d^2 positron configuration. Interelect.onic repulsion and interpositronic repulsion being similar ·both d^8 and d^2 electronic configurations give the same terms. A d^2 configuration is the hole equivalent of d^8. Note that a d^5 ion is i s own hole equivalent.

Hole formalism concept is useful in several areas:

1. The Russell Saunders terms of d^n ions are the same as those of their hole equivalents d^{10-n} ions.

2. Spin-orbit coupling constants (section 11.8) of less than half-filled subshell ions is positive while those of more than half-filled shells is negative. While for the less than half filled shells the coupling envisages some interaction between the positively charged nucleus and the electrons, the hole equivalents envisage interaction between the positive nucleus and an appropriate number of positrons. Hence the negative sign.

3. Because of the negative sign of the spin-orbit coupling constant (section 11.8) for more than half filled shells, the J levels of d^n ($n = 1-4$) become reversed for the corresponding hole equivalents. Thus the energy order of the J levels of d^2 ions is $^3F_2 < {}^3F_3 < {}^3F_4$ while that of d^8 is $^3F_4 < {}^3F_3 < {}^3F_2$.

4. Under the influence of the crystal filed the Russell Saunders terms undergo splitting. Sinee a positron is likely to be most stable where an electron is least so the crystal field splitting diagram of a d^n ion is reversed for its hole equivalent. Thus a $3d^9$ copper (II) may be regarded as a $3d^1$ positron case so that the positron will occupy the e_g set in octahedral field. The positron transition will then be $e_g \rightarrow t_{2g}$ instead of the $t_{2g} \rightarrow e_g$ electronic transition for $3d^1$ (electron) titanium (III) case.

11.8. SPIN-ORBIT COUPLING

Spin-orbit interaction energy is proportional to $ls \cos(ls)$ where l and s are the respective vectors. The strength of the coupling is decided by the proportionality constant known as the spin-orbit coupling constant ζ. ζ is relatively small ($\sim 50-800$ cm^{-1}) for the first transition series elements while for the lanthanides it is large (~ 1000 cm^{-1}). For the actinides spin-orbit coupling is so strong that the l and s vectors of the individual electrons couple to give j. The j's then combine to produce resultant J ($j-j$ coupling).

The magnitude of the spin-orbit coupling constant is given by :

$$\zeta = \frac{Z e^2 h^2}{8\pi^3 m^2 c^2 r^3}$$

where Ze is the nuclear charge, e, m and r are the charge, mass and radius of the orbit of the electron, h the Planck's constant and c the velocity of light. For a

multielectron system Z becomes Z_{eff} and λ refers to the spin-orbit coupling constant of a particular term:

$$\lambda = \pm \frac{\zeta}{2S} = \pm \frac{\zeta}{n}$$

where S and n represent the spin quantum number and the number of unpaired electrons of the term. The '+' sign refers to half-filled or less than half-filled shells while the '−' sign refers to more than half-filled shells. For a d^2 ion λ is '+' while for d^8—the hole equivalent of d^2—it is '−'. Remember that a proton attracts an electron but repels a positron.

11.9. RUSSELL SAUNDERS COUPLING AND LANDE INTERVAL RULE

The ^3F ground term of a d^2 free ion gives three J states: $^3F_2$, $^3F_3$ and $^3F_4$ (Fig. 11.8). The $^3F_2$ state is the ground state. The difference in energy of the J states is important for evaluation of magnetic moments, and is given by the *Lande Interval Rule. The energy separation between two immediate J states is given by the product of the spin-orbit coupling constant of the ion and the higher J.*

Just as each L has $2L + 1$ values of M_L and each S has $2S + 1$ values of M_S, each J has $2J + 1$ values of M^J. Thus the $^3F_2$ ground state (Fig. 11.8) has
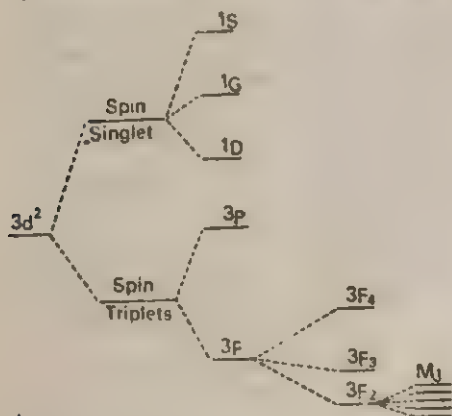
FIG. 11.8. Splitting of $3d^2$ ion under Russell Saunders coupling and a magnetic field. The figure shows in successive order:electron configuration, spin-spin coupling, *orbital-orbital coupling*, spin-orbit coupling and magnetic field splitting.
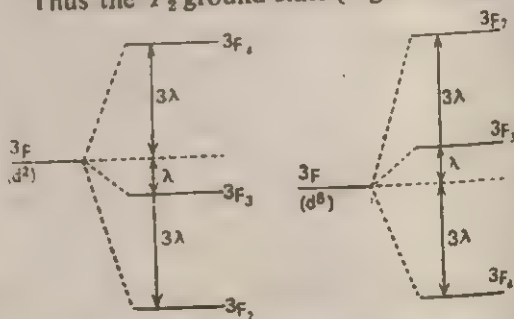
FIG. 11.9. Splitting of the terms of d^2 and d^6 by spin-orbit coupling.

M_J values $+ 2$, $+ 1$, 0, -1 and -2, On the application of the magnetic field each J state splits into $2J + 1$ levels of M_j, maintaining the pre-splitting baricentre. The following relations hold (Fig. 11.9):

d^2 ; $[(2 \times 4 + 1) \times 3\lambda] - [(2 \times 3 + 1) \times \lambda] - [(2 \times 2 + 1) \times (3 + 1)\lambda] = 0$

d^8 ; $[(2 \times 2 + 1) \times (3 + 1)\lambda] + [(2 \cdot 3 + 1) \times \lambda] - [(2 \times 4 + 1) \times 3\lambda] = 0$

For a d^8 system λ carries a negative sign which means the $^3F_4$ state (d^2) of Fig. 11.9 will be the most negative in energy i.e. the diagram of $3d^2$ will be reversed for $3d^8$ case.

11.10. ELECTRONIC SPECTRA AND CRYSTAL FIELDS

11.10.1. Group Theoretical Symbols : Each particular stereochemistry conforms to a particular mathematical group. Each mathematical group is characterised by symmetry elements and symmetry operations.

The metal ion orbitals respond to the group symmetry operations in different manner and they are designated by certain group theoretical symbols. These symbols may be upper case symbols (eg: A_{1g}, A_{2g}, E_g, T_{1g}, T_{1u} etc.) or lower case symbols (eg: a_{1g}, a_{2g}, t_{1g}, etc.). The lower case symbols are used to indicate one electron wave functions i.e. orbitals. Upper case symbols designate electronic states i.e. states arising out of interaction of electrons in different orbitals. Thus A_1g, T_1g, etc. stand for total many- electron interaction wave functions.

The symbols speak of degeneracies: A (or a) is singly degenerate, E (or e) is doubly degenerate while T (or t) is triply degenerate. Left hand superscript describes the spin multiplicity. Right hand subscript 'g' stands for 'gerade' (i.e. even) while 'u' stands for ungerade (i.e. uneven). Since an octahedron is centro-symmetric 'g' and 'u' are meaningful. A tetrahedron has no centre of symmetry and hence 'g' and 'u' subscripts are not used.

11.10.2. Crystal Fields in Relation to Russell Saunders Terms : When an ion becomes part of a complex it experiences an additional perturbation due to the crystal field. In Russell Saunders coupling the strength of the coupling varies in the order: spin-spin coupling > orbital-orbital coupling > spin-orbit coupling Depending on the strength of the crystal field, it can intercept the Russell Saunders coupling in several ways:

Case I. The crystal field is weaker than spin-orbit coupling. *J remains a good quantum number.* In such cases the ion behaves as if it were a free ion. Spectra and magnetic moments are not influenced by the crystal field.

Case II. The crystal field is stronger than spin-orbit coupling but weaker than orbital-orbital coupling. Such a field is known as *weak crystal field*. Weak field does not allow L and S vectors to couple to give J vectors; instead the terms due to orbital-orbital coupling are split further. *J is no longer a good quantum number.*

Case III. The crystal field is stronger than orbital-orbital coupling but weaker than spin-spin coupling. This is *medium field*.

Case IV. The crystal field is stronger than even the spin-spin coupling i.e. it is stronger than interelectronic repulsion. Such crystal fields force spin pairing and are known as *strong crystal field.*

Medium and weak crystal fields produce *high spin (spin free)* complexes while strong fields give *low spin (spin paired)* complexes. Weak crystal field dia-

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grams have been termed as Orgel diagrams. Tanabe-Sugano diagrams, to be shortly explained, give the relative energies of the Russell Saunders terms and crystal field terms on passing from weak to strong crystal fields.

11.10.3. Splitting of Russel Saunders terms in weak Crystal Fields : On the formation of a complex the degeneracy of the d-orbitals is lost. The degeneracy of the Russell Saunders terms of a free ion is thus lifted by the crystal field. The $3d^8$ nickel (II) ion has an F ground state with seven fold degeneracy ($2L + 1 = 2 \times 3 + 1$). In octahedral crystal field the F state splits into three states: A_2, T_2 and T_1 maintaining the total orbital multiplicity. *In crystal field splittings orbital multiplicity is conserved. Further the same spin multiplicity is retained on splitting* in weak field (Fig. 11.10).

An S state is like an s orbital which is singly degenerate and hence it cannot split. A P state is like p orbital and we have already seen that a p orbital cannot split in octahedral field. A P state thus merely changes notation to T_1. A D state is like d-orbitals and hence splits into T_2 and E states.

11.10.4. Tanabe Sugano Diagrams: Tanabe and Sugano have calculated the transition energies in going from weak to strong crystal field. The following points are relevant in connection with Tanabe-Sugano diagrams (Fig. 11.11).

1. The energies of the Russell Saunders terms appear on the ordinate and the crystal field strength ($\triangle = 10\ Dq$) as the abscissa.

2. d^1, d^2, d^3, d^8 and d^9 systems retain the same ground state no matter how strong the crystal field is. Recall that these are the ions which cannot admit of both the high spin and low spin forms *under the same octahedral geometry.* It is thus predicted that $3d^8$ nickel (II) cannot give diamagnetic octahedral complexes.

FIG. 11.10. Splitting of d^n ion Russell Saunders terms in weak octahedral crystal field. The ground state and the first excited state are shown.

3. d^4, d^5, d^6 and d^7 diagrams have a vertical line at a particular *critical* 10 Dq value. Above this particular critical 10 Dq value the ground state has a lower spin multiplicity. It is conventional to make this new ground state the abscissa so that all other terms have to be bent upwards by a corresponding amount. Recall that d^4, d^5, d^6 and d^7 are the four d^n systems which are capable of generating spin state equilibrium under the same octahedral geometry.

4. We can identify the spin allowed and spin forbidden transitions although all are Laporte forbidden. Taking the $3d^2$ case we see that $^3T_{1g}$ $(F) \rightarrow {}^3T_{2g}$, $^3T_{1g}$ (F) $\rightarrow {}^3A_{2g}$, $^3T_{1g}$ $(F) \rightarrow {}^3T_{1g}$ (P) are spin allowed while $^3T_{1g}$ $(F) \rightarrow {}^1T_{2g}$, $^3T_{1g}$ (F) $\rightarrow {}^1E_g$ are spin disallowed.

5. The splitting of a particular Russell Saunders term of a d^n ion is reversed for its hole equivalent d^{10-n} :

$$d^n \text{ (octahedral)} = \text{reverse of } d^{10-n} \text{ (octahedral)}$$

6. Since crystal field splitting of octahedral and tetrahedral fields are reverse of each other it follows that reversal of the octahedral crystal field term of a *particular Russell Saunders term* of a d^n ion will give the tetrahedral crystal field terms of the same d^n ion.

7. It follows from a combination of 5 and 6 that:

$$\text{octahedral } d^n \text{ terms} = \text{tetrahedral } d^{10-n} \text{ terms}$$
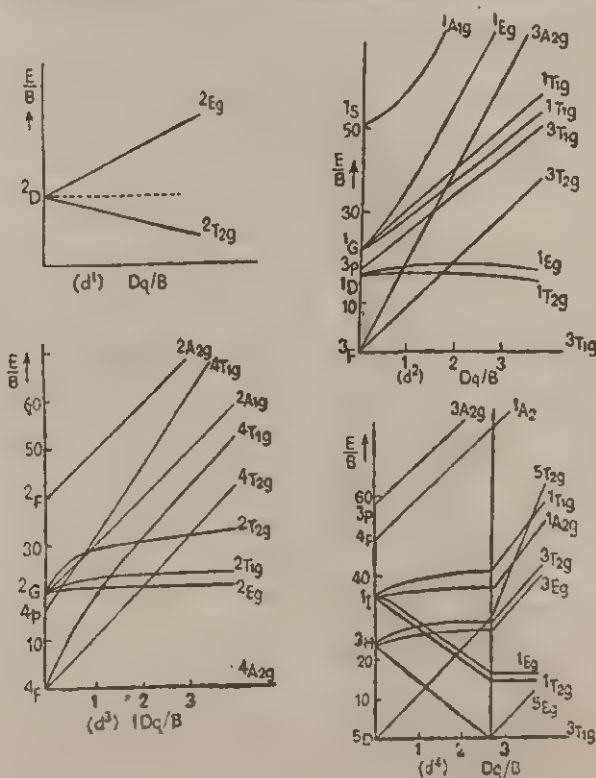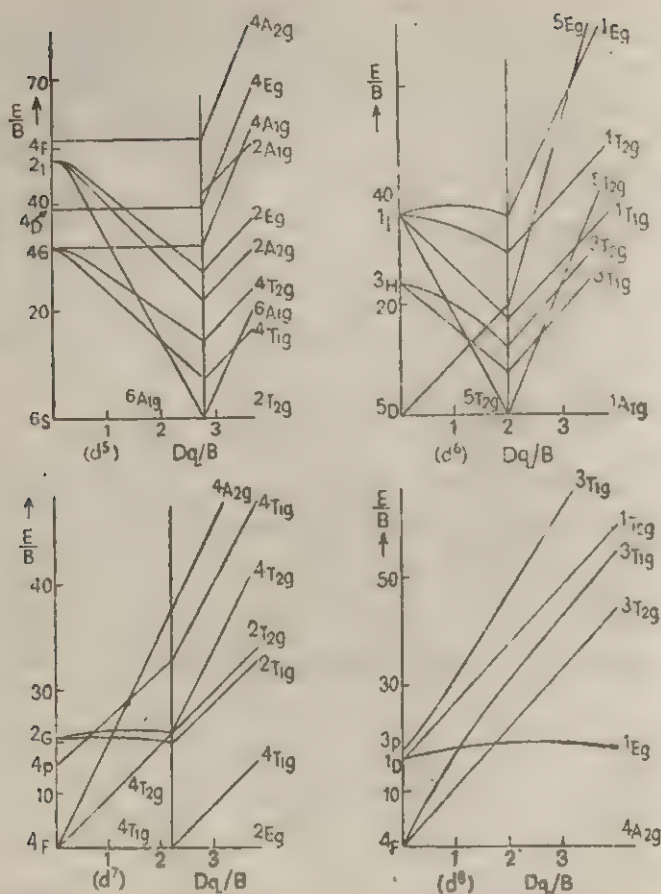
FIG. 11.11. Tanabe-Sugano diagrams of d^5 to d^8 ions in octahedral crystal fields.

However it should be remembered that 10 Dq_t is about 4/9 of 10 Dq (oct) for the same metal ion and the same ligand.

8. Since high spin d^5 gives $L = 0$. Russell Saunders terms of d^n and d^{5+n} are the same. Hence the splitting patterns of high spin d^{5+n} and d^n will be similar.

9. The energy separation of the various Russell Saunders terms are expressed in terms of interelectronic repulsion parameters known as Racah parameters B and C. The energy gaps between terms of the same spin multiplicity are multiples of B alone while the energy gaps between terms of different spin multiplicity are expressed as sums of multiples of both B and C. Thus the energy gap between ^3F and ^3P of a d^3 configuration is $15B$ while the difference between ^3F and ^1D is $5B + 2C$. In most cases C is close to $4B$. In complexes the free ion B values are reduced by $\sim 25\%$.

11.10.5. 10 Dq and B from Electronic Spectra : The $t_{2g} \to e_g$ (i.e. $d_{xy} \to d_{x^2-y^2}$) transition is called 10 Dq. We briefly describe how the relative energies of the different weak field transitions (Fig. 11.10) can be had. The ground state

of $3d^3$ is $^3T_{1g}$ (F) while the excited states with the same spin multiplicity are $^3T_{2g}$, $^3T_{1g}$ (P) and $^3A_{2g}$. There are two T_{1g} terms which develop some *configurational interaction* because of similar symmetry properties. Integral occupation of orbitals i.e. $^3T_{1g}$ (F) corresponding to t_{2g}^2 is not quite valid. Since there is only one $^3T_{2g}$ term it can be equated to the $t_{2g}^1 e_g^1$ configuration. The $^3A_{2g}$ term corresponds to e_g^2. When a crystal field term appears only once its energy, relative to the Russell Saunders term from which it is derived, is given by the one electron energies for each of the occupied d orbitals. Thus relative to $E(^3F) = 0$ the energies of the $^3T_{2g}$ term and the $^3A_{2g}$ terms are $(-4 + 6 = 2\ Dq)$ and $(+6 + 6 = 12\ Dq)$. Referring to Fig. 11.10 (d^2) and assuming that the $^3T_{1g}$ (F) is lowered by an amount x from the $^3F = 0$ baricentre, we have (y being 2 Dq) :

$$-3x + (3 \times 2)\ Dq + (1 \times 12)\ Dq = 0 \text{ so that } x = 6\ Dq = \tfrac{3}{5}\triangle.$$

The figures 3, 3 and 1 take into consideration the *orbital degeneracies* of the $^3T_{1g}$. $^3T_{2g}$ and $^3A_{2g}$ terms. The energy gap between ^3F and ^3P Russell Saunders terms is equal to $15B$ where B is the Racah interelectronic repulsion parameter. But in the case of a $3d^2$ complex from Fig. 11.10 we have:

$$^3T_{1g}\ (F) \rightarrow {}^3T_{1g}\ (P) = \tfrac{3}{5}\triangle + 15B'$$

where B' is now the interelectronic repulsion in the complex.

Not all the transitions are easily discernible from an actual spectrum of a complex. Furthermore the ratio of the different transition energies, intensities of the transitions, etc. are to be considered in order to identify an absorption band as a particular transition. Hexaaquovanadium (II),$[V(H_2O)_6]^{2+}$ ($3d^3$), gives three bands at 810 $m\mu$ (12,300 cm^{-1}), 540 $m\mu$ (18,500 cm^{-1}) and 360 $m\mu$ (27,900 cm^{-1}). These are assigned as: $^4A_{2g} \rightarrow {}^4T_{2g}$, $^4A_{2g} \rightarrow {}^4T_{1g}$ (F) and $^4A_{2g} \rightarrow {}^4T_{1g}$ (P). The lowest energy transition gives the 10 Dq value (12,300 cm^{-1}). Tris (ethylene-diamine) nickel (II) ($3d^8$) has the following spin allowed transitions: $^3A_{2g} \rightarrow {}^3T_{2g}$; $^3A_{2g} \rightarrow {}^3T_{1g}$ (F); $^3A_{2g} \rightarrow {}^3T_{1g}$ (P). It shows three absorption peaks: 910 mμ (11,000 cm^{-1}), 540mμ (18,500 cm^{-1}) and 335mμ (30,000 cm^{-1}), 11,000 cm^{-1} being the 10 Dq.

We can have now an exact example. Crystal field diagram of tetrahedral $3d^8$ (say, nickel (II)) will be the same as that of octahedral $3d^2$ system. For $[NiCl_4]^{2-}$ v_1, v_2 and v_3 will correspond to 8 Dq_t, 18 Dq_t, and 6 $Dq_t + 15B'$. v_2 and v_3 are experimentally 7,550 and 14.250 cm^{-1} respectively while v_1 remains unresolved. Free ion $15B'$ value is 16000 cm^{-1} whence B' then works out to be 780 cm^{-1}. Free ion 15B' value is 16000 cm^{-1} whence·B becomes 1066 cm^{-1}. *Thus on complexation a substantial reduction in interelectronic repulsion occurs. This is explained as a nephelauxetic effect* (cf. p. 241).

11.11. SOME QUANTITATIVE RELATIONS FOR PARAMAGNETIC SUBSTANCES

11.11.1. Curie Equation : Magnetic susceptibility of a substance is connected to its moment via Curie equation. In order to determine the magnetic suscepti-bility of a substance it has to be subjected to an applied magnetic field. The magne-tic field endeavours to bring about an alignment of the paramagnetic dipoles

with the direction of the field. On the other hand, temperature endeavours to disrupt this alignment. Thus the alignment of the magnetic dipoles will increase at low temperature and high field. An inverse relation between susceptibility and temperature thus exists.

Consider N (Avogadro number) paramagnetic centres each with a real magnetic moment μ. These paramagnetic entities will have a random distribution. On the application of magnetic field these will assume different orientations i.e. these will be at different angles with the field directions $\theta_1, \theta_2, \theta_3$, etc. Such a situation would mean that although each molecule has a real moment μ it is not shown up during measurement due to imperfect alignment with the field. A molecule (with a real moment μ) at an angle θ makes a contribution $\mu \cos \theta$ along H. Since different molecules make different contributions we assume that an average moment $\bar{\mu}$ is contributed by each molecule under the conditions of susceptibility measurements Then the following relations hold:

$$\chi_g = \frac{\chi_v}{\rho}; \quad \chi_M = \chi_g \times M = \frac{\chi_v}{\rho} \times M = \frac{I}{H} \times V$$

But $I = \dfrac{\text{molar magnetic moment}}{\text{molar volume}} = \dfrac{N\bar{\mu}}{V}$

$$\therefore \chi_M = \frac{I}{H} \times V = \frac{N\mu}{V \times H} \times V = \frac{N\bar{\mu}}{H}$$

Our problem is to derive a value for $\bar{\mu}$.

$\mu_\bullet$ = contribution towards $\bar{\mu}$ by the fraction of molecules at an angle θ with the direction of H.

     $= \mu \cos \theta \times$ fraction of molecules at an angle θ.

The fraction of molecules at an angle θ is determined by the difference in energy between two levels in relation to the prevailing thermal energy. Thus if n_0 and n_i are the number of molecules at the 0th and ith level and if $\triangle E$ is the energy difference between the two levels, then Boltzmann law states:

$$n_i = n_0 \exp(-\triangle E/kT) \quad \therefore \quad \frac{n_i}{n_0} = \exp(-\triangle E/kt)$$

If n_0 is large compared to n_i then n_i/n_0 represents the fraction of molecules.

Again on the application of a magnetic field there is a lowering in the energy of the magnetic dipoles:

$$\Delta E = -\bar{\mu}H$$

$\therefore \mu_\bullet = \mu \cos \theta \exp(-\Delta E/kT) = \mu \cos \theta \exp(\mu H \cos \theta \, kT)$
$\mu H \cos \theta$ is quite small compared to kT so that:

$$\mu_\bullet = \mu \cos \theta \left(1 + \frac{\mu H \cos \theta}{kT}\right)$$

An expression for μ can be had by summing over all possible orientations, taking into consideration the contribution of each orientation and its relative population. Thus $\bar{\mu}$, which is the average of μ_θ over all values of θ, is given by:

$$\bar{\mu} = \overline{\mu \cos \theta \left(1 + \frac{\mu H \cos \theta}{kT} \right)} = \overline{\mu \cos \theta} + \frac{\overline{\mu^2 H \cos^2 \theta}}{kT}$$

Average of $\cos \theta$ for all the molecules over a sphere is zero and that for $\cos^2 \theta$ is $\frac{1}{3}$. Thus:

$$\bar{\mu} = 0 + \frac{1}{3} \frac{\mu^2 H}{kT}$$

$$\therefore \ \chi_M = \frac{N\bar{\mu}}{H} = \frac{N\mu^2}{3kT} \quad \therefore \ \mu = \sqrt{\frac{3kT}{N\beta^2}} \cdot \chi_M = 2.84 \sqrt{\chi_M T} \quad \text{B.M.}$$

11.11.2. Thermal Energy and Magnetic Property : According to Russell Saunders coupling scheme a particular term carrying a given spin multiplicity and a given orbital multiplicity can assume several J values ranging between $|L + S|$ to $|L-S|$. A ^3F term can have J values 4, 3 or 2. The ^3F term can thus generate $^3F_4$, $^3F_3$ and $^3F_2$ states. Each of these states corresponds to a particular energy. The three states taken together constitute a multiplet and each J of a particular multiplet is a component of that multiplet. The energy difference between two successive J levels of the multiplet is called the multiplet width. Normally all molecules of a particular substance will tend to óccupy the lowest energy level but the actual population of the J levels will be dictated by the multiplet width of the levels compared to the thermal energy kT ($\sim$ 210 cm^{-1} at 300°K) available to the molecules. If the multiplet width is large compared to kT, very few molecules will have sufficient energy to populate the higher J level. Such considerations lead to three cases:

1. Multiplet width large compared to kT
2. Multiplet width small compared to kT
3. Multiplet width comparable to kT

1. *Multiplet width large compared to KT:* In such cases the multielectron L and S vectors couple very strongly so that the resultant lowest energy J is only populated. The other J levels are much above the ground state J and are not populated. The vector diagram of L and S coupling is shown in Fig. 11.12. The orbital angular momentum and spin angular momentum vectors are perpendicular to the plane of orbital motion and spinning motion, and the direction of the vectors is described by a screw motion (Chapter 1). Since positive current flows opposite to the direction of the electron motion, the direction of the magnetic moment vectors is opposite to the direction of the momentum vectors. Further since spin moment incorporates $g = 2$ as against $g = 1$ for the orbital moment, the μ_S has double the length of the S vector. However S vector and μ_L vector have the same length.

A strong coupling means a rapid precession of L and S about the direction of J, so that μ_L and μ_S also precess about J. Thus component BC (Fig. 11.12) averages to zero in any finite time. This means that μ_{LS} ($=$ AC vector) will be given by the vector AB.
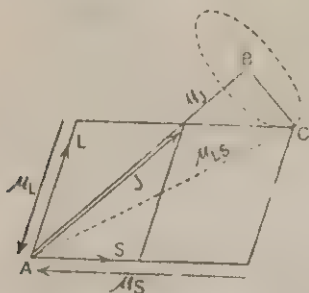
FIG. 11.12. Coupling of L and S to give J
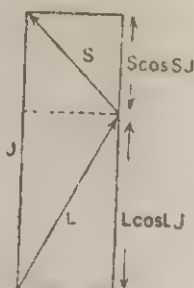
FIG. 11.13. Components of L and S along J

Components of L and S in the direction of J are respectively $L \cos (LJ)$ and $S \cos (SJ)$ (Fig. 11.13). Using cosine rule:

$$S^2 = J^2 + L^2 - 2LJ \cos (LJ)$$
$$L^2 = J^2 + S^2 - 2SJ \cos (SJ)$$

$$L \cos (LJ) = \frac{J^2 + L^2 - S^2}{2J} \text{ and } S \cos (SJ) = \frac{J^2 + S^2 - L^2}{2J}$$

The effective magnetic moment μ_J
$=$ Vector AB $=$ component of L in the direction of $J \div$ twice the component of S in the direction of J

$$= \beta L \cos (LJ) + 2\beta S \cos (SJ) = \left[\frac{J^2 + L^2 - S^2}{2J} + \frac{2(J^2 + S^2 - L^2)}{2J} \right] \beta$$

$$= \left[\frac{3}{2} + \frac{S^2 - L^2}{2J^2} \right] \beta J = g\beta J \text{ where } g \text{ denotes the quantity within the square}$$

bracket.

Putting the quantum mechanical relations we have:

$$S^2 = S(S + 1) \left(\frac{h}{2\pi} \right)^2 ; \quad L^2 = L(L + 1) \left(\frac{h}{2\pi} \right)^2 \text{ and } J^2 = J(J + 1) \left(\frac{h}{2\pi} \right)^2$$

where S, L and J are the respective quantum numbers. Therefore $\mu_J = g\beta \sqrt{J(J + 1)}$ where $g = 1 + \dfrac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)}$

Note that, when $S = 0$, i.e. no spin effect, then $g = 1$. The μ_J then reduces to μ_L. Again when $L = 0$, i.e. no orbital effect, then $g = 2$. The μ_J then reduces to μ_S.

The Curie equation now takes the form:

$$\chi_M = \frac{N\mu_J^2}{3kT} = \frac{Ng^2\beta^2 J(J + 1)}{3kT}$$

2. *Multiplet Width small Compared to kT* The multielectron system has now the J levels so close together that thermal energy can lead to a virtually equal population of all these levels. This means that the coupling of the L and S vectors is so poor that L and S vectors maintain their individuality. L and S are then said to interact independently with the field. *J is no longer a good quantum number.* The effective magnetic moment is then derived from the two separate contributions due to orbital effect and spin effect. Since magnetic susceptibility has an additive property the total susceptibility is given by:

$$\chi_M = \frac{N\mu^2_L}{3kT} + \frac{N\mu^2_S}{3kT} = \frac{N}{3kT}(\mu_L^2 + \mu_S^2)$$

Since $\mu_L^2 = L(L+1)\beta^2$ and $\mu_S^2 = 4S(S+1)\beta^2$

We have $\chi_M = \frac{N\beta^2}{3kT}[L(L+1) + 4S(S+1)]$

$$= \frac{N\mu^2_{L+S}}{3kT}$$

Therefore $\mu_{L,S} = \sqrt{L(L+1) + 4S(S+1)}\ \beta$

3. *Multiplet Width Comparable to kT*: Now the J levels of a multiplet are populated but not to the same extent. Their population is decided by Boltzmann distribution. The average susceptibility must be the weighted contributions and the final result becomes quite complicated with temperature dependence of the population.

For the wide multiplet case we have $\chi_M = \frac{Ng^2\beta^2}{3kT}J(J+1)$. Since the different J levels are populated the Avogadro number of molecules (N) will be distributed in these J levels. So χ_M will be given by a summation of terms of the following form where N_J is the number of molecules in a particular J level.

$$\chi_M = \Sigma\ \frac{N_J g_J^2\beta^2 J(J+1)}{3kT}$$

If the energy difference between the ground level (energy $= 0$) and a particular J level is $\triangle E$, then the number of molecules in the J level is proportional to $\exp(-\triangle E/kT)$. Each J has $2J+1$ orientations in a magnetic field (just as each l has $2l+1$ orientations of m_l) and therefore:

$N_J \propto (2J+1)\ \exp(-\triangle E/kT) \therefore N_J = C(2J+1)\ \exp(-\triangle E/kT)$ where C is a proportionality constant.

$$\chi_M = C\Sigma\ \frac{g_J^2\beta^2 J(J+1)}{3kT}(2J+1)\exp(-\triangle E/kT)$$

But $N = \Sigma N_J = C\Sigma\ (2J+1)\exp(-\triangle E/kT)$

Then $C = \frac{N}{\Sigma\ (2J+1)\exp(-\triangle E/kT)}$

and $\chi_M = \frac{\frac{N}{3kT}\ \Sigma\ g_J^2\beta^2 J(J+1)(2J+1)\exp(-\triangle E/kT)}{\Sigma\ (2J+1)\exp(-\triangle E/kT)}$

In order to be able to apply this equation we must not only know the L, S values and the different J values of the multiplet but also the energy difference $\triangle E$ between the ground level and the next higher energy J level. The energy difference is, according to Lande interval rule, given by:

Energy difference $= \lambda \times$ higher energy J value where λ is the spin-orbit coupling constant of the particular ion. For samarium ground state J is given by 5/2 and the higher J is 7/2. Therefore the energy difference between $J = 5/2$ and $J = 7/2$ is 7/2 λ where λ is the spin-orbit coupling constant of samarium. λ for samarium (III) is 236 cm^{-1}. Ground state g is 0.286 since $L = 5$ and $S = 5/2$. The first excited state g is 0.825. Then χ_M is (assuming population of the ground state and the first excited state):

$$\chi_M = \frac{N\beta^2}{3kT} \frac{(0.286)^2 \times \frac{5}{2} \times \frac{7}{2} \times 6 \exp(0) + (0.825)^2 \times \frac{7}{2} \times \frac{9}{2} \times 8 \exp(-\frac{7}{2}\lambda/kT)}{6 \exp(0) + 8 \exp(-\frac{7}{2}\lambda/kT)}$$

whence $\mu \simeq 1.3$ B.M. (kT at room temperature $\simeq 205$ cm^{-1}). Note that ground state J alone gives $\mu \to 0.84$ B.M. The experimental μ is $\simeq 1.5$ B.M.

Summing up the results of the three cases we have:

Multiplet width compared to kT	μ in B.M.	Temperature dependence of χ_M
1. Large	$g\sqrt{J(J+1)}$	Curie law obeyed
2. Small	$\sqrt{L(L+1)+4S(S+1)}$	,,
3. Comparable	complicated function of J and T	Curie law not obeyed

11.12. MAGNETIC MOMENTS OF THE FIRST TRANSITION SERIES IONS

11.12.1. General Observations: If for some reason the orbital effect is made negligible then the μ_{L+S} equation reduces to that of μ_S only:

$$\mu \text{ spin only } = \sqrt{4S(S+1)}\,\beta = \sqrt{2S(2S+2)}\,\beta = \sqrt{2ns(2ns+2)}\,\beta$$
$$= \sqrt{n(n+2)}\,\beta$$

where s is the spin quantum number of each electron (i.e. $\frac{1}{2}$) and n is the number of unpaired electrons. For most of the ions of the first transition series it is found that in their complexes the magnetic moment is that due to spin effect alone. Table 11.4 gives some such results.

It will be noted from the Table that in some cases the observed moments are higher than spin only moments but rarely do the values approach the μ_{L+S} moments. This is due to the crystal fields (that is, the ligands surrounding the ions) restricting the movement of the metal ion electrons around the nucleus. The orbital effect is thus often negligible. Quantitative derivations have been made of the crystal field effects on the magnetic moments of the first series transition elements, particularly for Co^{3+} (tetrahedral) and Ni^{2+} (octahedral) complexes.

Table 11.4. Calculated and Observed Magnetic Moments of the Transition Series Ions

Ion	Ground State Quantum Numbers		Spectro-scopic Symbol	μ_J B.M.	μ_S B.M.	μ_{L+S} B.M.	Observed moment (B.M.)
	S	L					
$V^{4+}(3d^1)$	$\frac{1}{2}$	2	$^2D_{3/2}$	1.55	1.73	3.00	1.6—1.8
$V^{3+}(3d^2)$	1	3	$^3F_2$	1.63	2.83	4.47	2.6—2.8
$Cr^{3+}(3d^3)$	$\frac{3}{2}$	3	$^4F_{3/2}$	0.77	3.87	5.20	3.7—3.8
$Cr^{2+}(3d^4)$	2	2	$^5D_0$	0	4.90	5.48	4.9—5.3
$Mn^{2+}(3d^5)$	$\frac{5}{2}$	0	$^6S_{5/2}$	5.92	5.92	5.92	~ 5.9
$Fe^{2+}(3d^6)$	2	2	$^5D_1$	6.70	4.90	5.48	5.1—5.5
$Co^{2+}(3d^7)$	$\frac{3}{2}$	3	$^4F_{9/2}$	6.64	3.87	5.20	4.1—5.2
$Ni^{2+}(3d^8)$	1	3	$^3F_4$	5.59	2.83	4.47	2.8—4.0
$Cu^{2+}(3d^9)$	$\frac{1}{2}$	2	$^2D_{5/2}$	3.55	1.73	3.00	1.7—2.2

11.12.2. Orbital Rotation and Transformation Model: We assume an electron both as a particle and as a wave. On the solar model we assume an electron as a particle moving in an orbit around the nucleus. While doing so the electron generates orbital magnetic effect in addition to the spin effect. According to the wave model the electron has to stay in orbitals of a definite size and shape. When a transition metal ion forms a complex its d-electrons are in a crystal field of the surrounding ligands. Such a d^n ion can give rise to orbital moment in addition to spin moment only if its electrons are allowed unrestricted movement from one orbital to another so as to effect a rotation about the metal ion nucleus. For this to be possible the following conditions must be fulfilled:

1. *The orbitals must be degenerate else there will be an energy barrier for rotation.*
2. *The orbitals must be of the same shape and they must be transformable from one to another by rotation about a suitable axis.*
3. *The orbitals should not contain electrons of the same spin.*

In a crystal field the degeneracy of the d-orbitals is lost. This immediately tells us that the full orbital contribution of a free ion may not be attained when the ion forms a coordination complex. The e_g ($d_{x^2-y^2}$, d_{z^2} orbitals) set in octahedral geometry or the e set in tetrahedral geometry, although degenerate, is different in energy from the t_{2g} set (or t_2 set) and furthermore the d_{z^2} orbital is not transformable into any of the other four orbitals. So electrons in e_g or e level cannot make orbital contribution to the spin moment. Thus $d_{x^2-y^2}$ and d_{z^2} orbitals constitute a non-magnetic doublet. Each of the d_{xy}, d_{yz} and d_{zx} orbitals is transformed into the other two orbitals by rotation about relevant axes eg: d_{xy} gives d_{yz} on rotation about x axis. Presence of electrons in the t_{2g} set (or t_2) will generate orbital contribution provided condition 3 is satisfied. d^1 and d^2 complexes will generate orbital moment as all the three conditions are satisfied. But d^3 in octa-

hedral geometry violates condition 3 while in tetrahedral stereochemistry all the conditions are satisfied ($e^2:t_2^1$). In high spin octahedral forms d^1, d^2, d^6, d^7 will have orbital moment but not in tetrahedral geometry. Magnetic moments in excess of spin only values may often be diagnostic of stereochemistry. Our model predicts spin-only value for $3d^8$ nickel (II) in octahedral geometry and for $3d^7$ cobalt (II) in tetrahedral stereochemistry. Table 11.4, shows, however that both these metal ions possess considerable orbital effect.

The eight electrons of octahedral nickel (II) can be arranged in only one way, $t_{2g}^6 eg^2$, giving a singlet state $^3A_{2g}$. The first excited state is $t_{2g}^5 eg^3$ giving a triplet $^3T_{2g}$ and the second excited state is $t_{2g}^4 eg^4$ again giving a triplet $^3T_1$. Both the excited states can produce orbital moment. The smaller 10 Dq is the closer $^3T_{2g}$ is to $^3A_{2g}$ and the greater is the scope that spin-orbit coupling will mix the two states producing above-spin only moments. Similar reasoning will apply for tetrahedral cobalt (II) with $^4A_2$ ground state and $^4T_2$ first excited state. The quantitative relation connecting magnetic moment and spectral transitions is given by:

$$\mu = \mu_{spin\ only}\left(1 - \alpha\frac{\lambda}{10\ Dq}\right)$$

where $\alpha = 2$ for an E ground term and $\alpha = 4$ for A_2 terms, 10 Dq is the separation between the ground and excited states and λ is the spin-orbit coupling constant of the term.

A and E states do not produce orbital moment but a T state does. Further, the loss of degeneracy of the d-orbitals results in a diminished orbital effect and thus, the lower the symmetry of the complex the closer the magnetic moment is to the spin-only value.

11.13. MAGNETIC PROPERTIES OF THE RARE EARTHS (LANTHANIDES)

The electron distributions of the rare earths have been shown in Chapter 2. The trivalent rare earth ions have incomplete 4f shell which is the source of their magnetism. Their 4f shell is quite deep seated and is shielded from the disturbing effects of surrounding ions (crystal field effect). The trivalent rare earth ions therefore behave as perfect ions. Furthermore the J levels are widely separated due to strong coupling of L and S vectors. They conform to the case of wide multiplet widths compared to kT, so that their magnetic moments are obtained by the equation:

$$\mu_J = g\beta\sqrt{J(J+1)} \text{ where } g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

There are only two exceptions (Table 11.5), namely samarium (III) and europium (III) where the J levels have multiplet widths comparable to kT. For promethium (III) the separation between $J = 4$ and $J = 5$ is given by 5 λ($= 5 \times 400$ cm^{-1}) while for samarium (III) the first excited state is $7/2 \times 236$ cm^{-1} above the ground state. For europium the first excited state is only λ ($= 220$ cm^{-1}) above the ground

state. It is thus likely that the first excited state in Sm^{3+} and particularly in Eu^{3+} will be substantially populated. For Eu^{3+} even the second excited state will have significant population. In these two cases the complicated susceptibility equation for the multiplet width comparable to $kT(\sim 205 \text{ cm}^{-1}$ at $25°C)$ must be applied. When this is done the magnetic moments of all the fourteen rare earths fit nicely with experimentally determined moments. The double humped curve is shown in Fig. 11.14. Note that μ spin-only does not apply except for f^0, f^7 and f^{14} systems. In these three cases $L = 0$ (i.e. $S = J$) so that μ_J equation automatically reduces to μ spin-only equation.
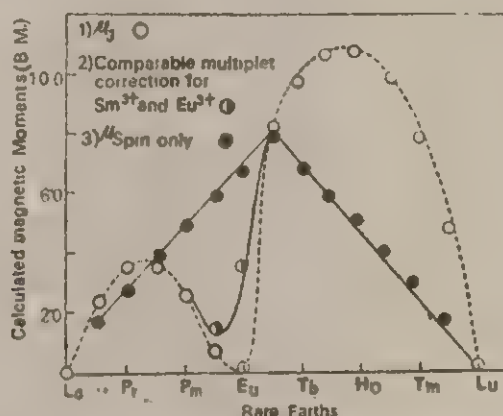
FIG. 11.14. Calculated magnetic moments of the rare earths

Table 11.5. Magnetic Moments of Rare Earths

4f electrons	M^{3+} ion	Ground State	g	Calculated $\mu = g\beta \sqrt{J(J+1)}$	Experimental μ(B.M.)
0	La	$^1S_0$	—	0	Diamagnetic
1	Ce	$^2F_{5/2}$	6/7	2.54	2.3—2.5
2	Pr	$^3H_4$	4/5	3.58	3.4—3.6
3	Nd	$^4I_{9/2}$	8/11	3.62	3.5—3.6
4	Pm	$^5I_1$	3/5	2.68	—
5	Sm	$^6H_{5/2}$	2/7	0.84	1.5—1.6
6	Eu	$^7F_0$	—	0	3.4—3.6
7	Gd	$^8S_{7/2}$	2	7.94	7.8—8.0
8	Tb	$^7F_6$	3/2	9.72	9.4—9.6
9	Dy	$^6H_{15/2}$	4/3	10.63	10.4—10.5
10	Ho	$^5I_8$	5/4	10.60	10.3—10.5
11	Er	$^4I_{15/2}$	6/5	9.57	9.4—9.6
12	Tm	$^3H_6$	7/6	7.63	7.1—7.4
13	Yb	$^2F_{7/2}$	8/7	4.50	4.4—4.9
14	Lu	$^1S_0$	—	0	Diamagnetic

11.14. MAGNETIC PROPERTIES OF FIRST TRANSITION SERIES IONS ON VALENCE BOND AND CRYSTAL FIELD MODELS

We have discussed the two theories for transition metals in Chapter 10. We have seen that although qualitatively VB theory can explain many magnetic properties, yet it is quantitatively inadequate. However we discuss two examples on the two models. For example, the magnetic moments of $Na_3[FeF_6]$ and $K_3[Fe(CN)_6]$ are 5.92 and 1.73 B.M. both being complexes of iron (III). The fluoro complex indicates five unpaired spins and the cyano complex only one. According to VB theory the fluoro complex is an outer orbital complex with sp^3d^2 hybridisation of iron (III) orbitals leaving all five $3d$ orbitals available to the five unpaired electrons of iron (III). It is said to be a weak complex. On the other hand the cyano complex is a strong inner orbital complex with d^2sp^3 hybridisation of iron (III) orbitals. Only three of the five $3d$ orbitals are available for five electrons of iron (III). Hence spin pairing occurs and the complex shows only one unpaired spin.

In crystal field terms we say F^- is a weak ligand and hence 10 Dq is smaller than pairing energy. Therefore all five electrons distribute between t_{2g} and e_g levels without spin pairing. On the contrary CN^- is the strongest ligand known, splitting being large (10 $Dq > P$). So spin pairing occurs and all five electrons are forced to stay in the three t_{2g} orbitals, one remaining unpaired.

Problem: Predict the spin magnetic moment of $K_3[Mn(CN)_6]$

Note that cyanide is a monodentate ligand and that the oxidation state of manganese is $+3$. Trivalent manganese has $25-3 = 22$ electrons i.e. it is a $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$ or simply a $3d^4$ system. So we have to examine the spin moment (orbital magnetic moment is neglected) of a $3d^4$ ion in octahedral geometry. The question now is whether the complex will be high-spin or low-spin. Since cyanide is the strongest ligand it will generate an inner orbital octahedral complex i.e. the hybridisation will be $d^2 sp^3$. Hence 4 electrons will stay in the three non-bonding d orbitals. So according to Hund's rule we will have two unpaired electrons:

3d	4s	4p
↑↓ | ↑ | ↑ | xx | xx	xx	xx | xx | xx ; $\mu = 2.83$ B.M.
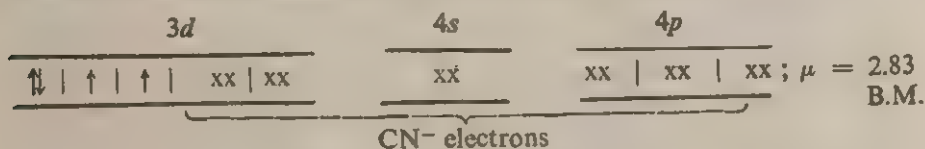
CN⁻ electrons

In crystal field terminology the complex will be low-spin octahedral i.e. $t^4_{2g} e^0_g$, once again there will be two unpaired electrons. The spin magnetic moment will be around 2.83 B.M.

Problem: Predict the spin magnetic moment of $Li[Ti(dipy)_3]$

Note dipyridyl is a neutral bidentate ligand. Stereochemistry around titanium (-1) is octahedral. Uninegative titanium has a total of 23 electrons. It is a $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ i.e. a $3d^5$ system. Taking dipyridyl as a strong ligand we assume

that the complex is an inner orbital octahedral complex. Hence the five non-bonding electrons will be arranged in the three of the five d-orbitals which are not participating in the hybridisation process. Then one unpaired electron with spin moment 1.73 B.M. will show up. According to crystal field theory it will be a low-spin complex i.e. $t^5_{2g} e^0_g$. Once again there will be one unpaired electron with spin moment 1.73 B.M.

Problem: Bis (dimethylglyoximato) nickel (II) is experimentally known to be diamagnetic. How do we interpret on VB and CF models ?

Note dimethylglyoximate ion (section 10.16.1) is a bidentate ligand. Hence the coordination number of nickel (II) is four. When C. N. is four two stereochemistries namely tetrahedral and square planar are possible. Since tetrahedral geometry is possible only with weak coordinating ligands, we safely exclude this geometry.

In VB model a square planar geometry means a dsp^2 hybridisation. Again bipositive nickel is a $3d^8$ system. Hence these eight electrons will be arranged in the four non-bonding d-orbitals and according to Hund's rule all eight will be paired up. Hence the diamagnetism.

In crystal field model we can no longer take the octahedral splitting. We have to go for the tetragonally elongated or square planar splitting:

$$d_{xz}, \ d_{yz} < d_{z^2} < d_{xy} < d_{x^2-y^2}$$

If the separation between the highest two orbitals (d_{xy} and $d_{x^2-y^2}$) is large compared to the pairing energy of nickel (II) then all eight electrons will get paired, giving a diamagnetic complex. Since this is an experimentally observed fact that the complex is a diamagnetic one the obvious conclusion is that dimethylglyoxime is a strong field ligand.

Problem: Predict the number of unpaired electrons in $[CoCl_4]^{2-}$.

Since chloride ion is a monodentate ligand and since there are four of them in the coordination zone the geometry may be tetrahedral or square planar. But chloride ion is a very weak ligand and hence square planar stereochemistry is ruled out. For tetrahedral stereochemistry VB theory predicts sp^3 hybridisation. So cobalt (II) being a $3d^7$ ion its seven electrons will be housed in the five $3d$ orbitals. According to Hund's rule only three electrons will remain unpaired. In crystal field model the complex has to be high spin and the electron distribution will be $e^4 t_2^3$ so that three electrons will remain unpaired.

11.15. DETERMINATION OF MAGNETIC SUSCEPTIBILITY

A number of methods are known for the purpose. Gouy method is the most commonly used technique. The sample, in the form of a cylinder, is suspended between the poles of a magnet, preferably an electromagnet. The bottom of the substance coincides with the centre of the magnetic field, and the substance extends to a length of about 10 cm such that the magnetic field is zero at the upper point. The sample is packed uniformly into a glass tube of suitable size and is vertically

suspended from the beam of a balance in a drought free enclosure (Fig. 11.15). The mass of the sample is determined with and without the magnetic field on. Similar determination is also carried out with the same sample tube so as to allow for a diamagnetic correction of the glass tube.
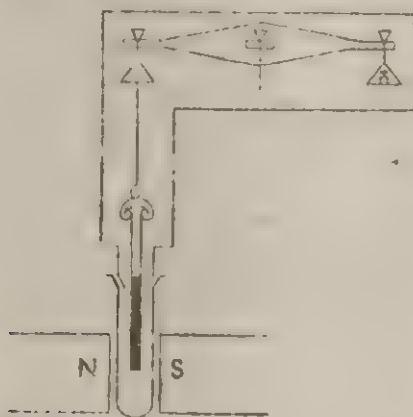
FIG. 11.15. Apparatus for the Gouy method

A magnetic sample is composed of innumerable micromagnets with random orientation. On the application of a magnetic field there is an alignment of the micromagnets with the field. If the sample were in the form of a very small sphere at the centre of a uniform magnetic field there would be no net force acting on it. Instead if it is suspended in the form described above its lowest part would be in the strongest field while the topmost part will be in a weak or zero magnetic field. Hence there will be a net magnetic force acting on the cylindrical sample. As a result of this a paramagnetic sample will be drawn into, while a diamagnetic sample will be drawn out of the strongest part of the magnetic field. Also note that the derivation of the χ_g by the Gouy method involves two limits of the magnetic field between which the force is integrated.

The small force dF experienced by a sample of volume susceptibility κ and small volume dv in a magnetic field H is given by:

$$dF = H.\kappa\, dv\, \frac{dH}{dx} \quad \text{where } \frac{dH}{dx} \text{ is the field gradient.}$$

$$= H.\kappa.A.dx.\frac{dH}{dx} \quad \text{where } A \text{ is the cross-sectional area and } dx \text{ is}$$

the small height of the sample.

$$\therefore dF = A.\kappa.HdH$$

Intergrating, $F = \displaystyle\int_{H_0}^{H} dF = \int_{H_0}^{H} A.\kappa.HdH = A.\kappa.\frac{1}{2}(H^2 - H_0^2)$

where H and H_0 are the lower and upper limits of the magnetic field.

$$F = A. \chi_g \cdot \rho \tfrac{1}{2} (H^2 - H_0^2) \left(\text{recalling that } \chi_g = \frac{\kappa}{\rho} \right)$$

$$= \chi_g \cdot \frac{m}{l} \cdot \tfrac{1}{2} (H^2 - H_0^2) \text{ where } m \text{ and } l \text{ stand for the mass and}$$

length of the sample. $\left(\rho = \dfrac{m}{A.l} \right)$

Simplifying further that H_0 can be neglected we have:

$$\chi_g = \frac{2l \times F}{H^2 \times m}$$

Force F is determined by the change in the weight of the sample i.e. by the product of w (the change in mass of the sample in the magnetic field) and g, the acceleration due to gravity. The change in the mass of the sample is the sum of the apparent change of mass of the sample in the magnetic field and the change of mass of the empty glass tube. Then:

$$\chi_g = \frac{2l \, wg}{H^2 \times m} = \frac{2l \text{ (in cm)} \times w \text{ (in gm)} \times 981}{H^2 \text{ (in gauss)} \times m \text{ (in gm)}}$$

Some people prefer to express w in milligrams and m in gm so that

$$\chi_g = \frac{2l \text{ (in cm)} \times w \text{ (in milligram)} \times 10^{-3} \times 981}{H^2 \text{ (in gauss)} \times m \text{ (in gm)}}$$

$$= \frac{2l \text{ (in cm)} \times w \text{ (in milligram)}}{H^2 \text{ (in gauss)} \times m \text{ (in gm)} \times 1.019}$$

Since H is of the order of 10^3 our final χ_g will come out in the order of 10^{-6} cgs units.

$$\chi_M = \chi_g \times M \text{ where } M \text{ is the molecular weight}$$

The quantity $\dfrac{2l}{H^2}$ is called the *tube calibration constant*. The tube constant is first determined by taking a measurement on a standard substance, such as, copper (II) sulphate pentahydrate ($\chi_g = 5.92 \times 10^{-6}$ cgs units), [Hg Co(SCN)$_4$] ($\chi_g = 16.44 \times 10^{-6}$ cgs units), for which χ_g is accurately known. The same tube is then cleaned and used to determine the χ_g of the substance under investigation. For paramagnetic substances the above χ_M is corrected for the diamagnetism of the ligands using Pascal's constants. The corrected χ_M is then used to calculate the magnetic moment with the help of the Curie equation. Table 11.5 gives some spin only magnetic moments for various numbers of unpaired electrons alongwith the corresponding susceptibilities.

Table 11.6. Spin only Susceptibilities and Moments for 1-5 Unpaired Electrons

Unpaired electrons	$2S + 1$	μ spin only	χ_M (corrected) (cgs units)
1	2	1.73 B.M.	$1,250 \times 10^{-6}$
2	3	2.83	3,333
3	4	3 87	6,250
4	5	4.90	10,000
5	6	5.92	14,600

STUDY QUESTIONS

1. $(NH_3)_3[FeF_6]$ has a magnetic moment of 5.92 B.M. whereas $K_3[Fe(CN)_6]$ has a value of 1.73 B.M. Explain both on the valence bond model and the crystal field model.

2. Guess the magnetic moments of $[Ti(dipy)_3]$ and $Li[Ti(dipy)_3]$.

3. Molybdenum (V) is a $4d^1$ system. $(NH_4)_2[MoOCl_6]$ is paramagnetic $(\mu \sim 1.7$ B.M.) but $[MoO_2Q.py]$ is diamagnetic (QH = quinaldinic acid). Chemical studies show that in $[MoO_2Q.py]$ we still have a pentavalent molybdenum. How would you explain this anomalous magnetic behaviour?

4. Transition metal compounds are often paramagnetic whereas non-transition metal compounds are diamagnetic. Comment.

5. Strong ligands are most likely to enforce spin pairing. Comment. Show on the crystal field model that it may be possible to synthesize complexes with some ligands where magneto-chemical equilibrium between high spin and low spin forms of the same complex may exist.

6. What is meant by the symbol ^3F? Snow that it represents a total degeneracy (orbital plus spin) of 21.

7. In general elements of the second and third transition series form more spin paired complexes than elements of the first transition series of the same group. Attempt an explanation based on the relative sizes of the orbitals.

8. Account for the following magnetic moments observed in various complexes

$$V^4{+}1.7 \text{ to } 1.8; \ V^3{+} 2.6 \text{ to } 2.8; \ Gd^3{+} 7.94 \text{ B.M.}$$

9. The brown ring compound has the following structure in aqueous sulphuric acid medium, $[Fe(NO)(H_2O)_5]SO_4$. The magnetic moment is 3.90 B.M. What will be your guess about the valence of iron in this compound on spin-only considerations?

10. Comment on the following magnetic susceptibilities: (a) $K_3[CoF_6]$ has $\mu = 4.2$ B.M. but $K_3[CuF_6]$ has 2.8 B.M. and $K_2[NiF_6]$ is diamagnetic.

(b) monovalent silver (coordination number = 2) is diamagnetic, bivalent silver (C.N. 4 and 6) is paramagnetic $(\sim 1.7$ B.M.) and trivalent silver (C.N. 4) is again diamagnetic.

11. Calculate the magnetic moment of an ion with $^3F_4$ ground state following the μ_J, μ_S and μ_{L+S} equations. What will be the ground state of its hole equivalent? Calculate the moments of the hole equivalent.

12. Explain why the μ_J equation is not applicable to Sm^{3+} ($4f^5$) and Eu^{3+} ($4f^6$) although it is quite good both for Pr^{3+} ($4f^2$) and Tb^{3+} ($4f^8$).

13. How is the orbital moment quenched in most of the first transition series complexes? Why the quenching is not perfect in nickel (II) in octahedral field and cobalt (II) in tetrahedral field?

14. What do you understand by spin-orbit coupling constant? What factors govern its magnitude? How does it influence the magnetic moments of lanthanides and the first transition series?

15. (a) What informations can be had from the following relation:

$$X_{dia} = - \frac{Ne^2}{6mc^2} \Sigma \overline{r^2}$$

(b) Discuss the usefulness of Pascal's constants.

16. A d^2 ion has the energy sequence $^3F_2 < ^3F_3 < ^3F_4$. What is the energy sequence of a d^8 ion?

17. What informations do the following symbols provide?

(a) $^4T_{1g}$ (b) $^6A_1$ (c) ^3P

18. In which of the stereochemistries a d^8 ion is likely to have orbital contribution: (a) tetrahedral, (b) octahedral and (c) square planar. What is the maximum magnetic moment this ion can give rise to?

19. Comment on the stereochemistry of the following cobalt (II) complexes based on magnetic moments: $[Co(SCN)_4]^{2-}$, 4.40 B.M.; CoI_2 (aniline)$_2$, 4.61 B.M.; $CoCl_2$ (aniline)$_2$ (EtOH)$_2$, 5.0 B.M. and $CoCl_2.6H_2O$, 5.1 B.M.

20. Is it possible to synthesize a complex of a d^4 ion with μ ~ 2.83 B.M. with octahedral or tetrahedral geometry?

21. Give valence bond and crystal field explanation of the spin magnetic moment of $K_3[Mn(CN)_6]$ being 2.8 B.M.

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Radioactivity

12.1. THE BEGINNING

In science time and again chance has favoured a prepared mind. Becquerel had a prepared mind to make most of a chance observation made in 1896. He was at the time interested in discovering some connection between X-rays and fluorescence phenomena exhibited by certain chemical compounds. Fluorescent substances absorb energy when exposed to sources of radiation, but thereafter emit energy of a nature different from that of the incident radiation. Potassium uranyl sulphate was considered at Becquerel's time as a fluorescent substance. Becquerel planned to expose some samples of this compound to sunrays, and thereafter to examine the effect of the emitting radiations on photographic plates. As it happened for a few days in a row the sky was overcast, and the sun did not show up. Consequently the samples of potassium uranyl sulphate exposed to the atmosphere on those cloudy days did not receive the expected radiations from sunrays, and in keeping with the ideas prevalent at that time, none of the samples was expected to show any fluorescence effect on photographic plates. But Becquerel was a physicist of the first order and he did not leave the experiments unfinished. Some photographic plates were exposed to the samples, were developed, and he was astonished to see that the plates were affected as much as those exposed for an equal length of time to bright sunlight. He then packed his samples in closed cupboards in the dark and studied them further. Photographic plates were equally affected, and the conclusion was that the samples were themselves active, and need not to be excited by external sources of radiation. It was also shown that potassium sulphate had nothing to do with this behaviour. So Becquerel made a most remarkable observation that uranium spontaneously emits a powerful radiation whose existence had not previously been suspected. *The phenomenon of emission of radiations as a result of spontaneous disintegrations of atomic nuclei was termed radioactivity.*

Thus radioactivity made a bright beginning on not-so-bright a day in 1896.

Further studies by Becquerel showed that all uranium compounds were radioactive, and that the rate of emitting radiation was directly proportional to the amount of uranium present in the sample. However an exception to the rule was soon discovered. A uranium containing ore, called pitchblende, emitted radiation at a rate nearly four times as great as one would calculate on the basis of its uranium content alone. In 1896 Becquerel in collaboration with two illustrious young colleagues Marie and Pierre Curie, successfully isolated a fraction of a gram of a new element, called polonium, from a ton of pitchblende ore. Polonium was much more radioactive than uranium, and thus the exceptional behaviour of pitchblende was explained. Within a year of discovery of polonium, the Curies discovered radium, another highly radioactive element. Recognition of the services to science came soon. Becquerel and the Curies were awarded the Nobel Prize in Physics in 1903.

The radioactivity associated with naturally occurring materials, such as uranium, polonium, radium etc. is called natural radioactivity. It was later shown by Irene Curie, daughter of the Curies, and her husband Joliot-Curie that radioactivity can also be induced by suitable artificial transmutation reactions carried out on non-radioactive elements. Such artificially created radioactivity is called artificial radioactivity.

12.2. THE NATURE OF THE RADIATIONS

Painstaking reasearches followed Becquerel's chance discovery of radioactivity in uranium. The Curies, and Rutherford played significant roles in these scientific pursuits. The radiations emanating from radioactive substances were subjected to elaborate investigations in magnetic and electric fields. Researches revealed the startling concept that radioactivity was a nuclear effect. Some atomic nuclei undergo spontaneous and sudden change, and release charged particles which are accompanied by radiant energy in the form of gamma rays.

The radiations emitted by naturally radioactive elements were shown to be split by an electric or magnetic field into three distinct parts: alpha, beta and gamma rays.

12.2.1. Alpha Rays: These consist of a stream of positively charged particles, called alpha particles, which carry a $+ 2$ charge and have a mass number 4. These particles were shown by Rutherford to be identical with the nuclei of helium atom, that is, these are doubly charged helium ions He^{2+} (atomic number 2, mass number 4).

The characterization of the alpha particles was based on several experimental results. The ratio of charge to mass of alpha particles was determined by a study of the deflection of their path in superimposed electric and magnetic fields, as was done by Thomson for characterization of electrons. Such experiments provided a value of 4.8×10^3 e.m.u. units (1 $e.m.u. = 3 \times 10^{10}$ $e.s.u.$) per gm and the value was independent of the source of the alpha particles. This e/m is almost half the e/m of proton. This means if the alpha particle carries a single charge like the

proton its mass must be twice as large. Instead, if the alpha particle carries two units of charge then its mass must be four times as large as that of the proton. The matter was settled through independent measurements of the charge of the alpha particle, the magnitude of which was shown to be twice as large (9.3×10^{-10} e.s.u.) as that of the electron (4.8×10^{10} e.s.u./electron). Therefore an alpha particle has to have two units of positive charge and four units of mass, that is, it is a doubly charged helium ion.

Finally its identity with helium ion was shown by another novel experiment done by Rutherford. A quantity of purified radon gas, an alpha emitter, was placed in a thin walled tube A (Fig. 12.1). The tube A was sealed into another tube T connected to another spectrum tube S with arrangement for passing electric discharge. The tube T was evacuated, and after a few days the gas collected inside T was compressed by raising the mercury level. On passing a discharge in the tube S, the spectrum of helium was obtained. Control experiments showed that ordinary helium gas cannot pass through the walls of A into T. Alpha particles, however, are able to do so. Thus the identity of the alpha particles as He^{2+} was established.

When an alpha particle is ejected from within the nucleus, the nucleus of the mother element loses two units in atomic number, and four units in mass number. For instance, on ejection of an alpha particle by uranium nucleus (atomic number 92, mass number 238), the nucleus of the daughter element will have an atomic number 90 and a mass number 234. Checking from the Periodic Table we can conclude that the daughter element will be an isotope of thorium, which also has an atomic number 90. This nuclear reaction is represented as:

FIG. 12.1. Apparatus for detection of helium in decay of radon

$$_{92}^{238}U \rightarrow {}_2^4He + {}_{90}^{234}Th$$

In nuclear reactions the residual charges on the different species are ignored and the equations are designed to express only the reactant nuclei and the product nuclei. However in such equations both the atomic number and the mass number must be balanced.

12.2.2. Beta rays: These are made up of a stream of negatively charged particles (beta particles). They have been shown to be identical with electrons from a study of their behaviour in electric and magnetic fields and from a study of their e/m values (1.77×10^8 coulombs/gm). The ejection of a beta particle (charge -1, mass 0) results from the transformation of a neutron (mass 1, charge 0) somewhere at the surface of the nucleus into a proton (mass 1, charge $+1$).

$$_0^1n \rightarrow {}_1^1H + {}_{-1}^0e$$

Consequently when a beta particle is emitted from the nucleus, the daughter

element nucleus has an atomic number one unit greater than that of the mother element nucleus. An instance of spontaneous beta emission is observed in the transformation of thorium—234 (atomic number 90, mass number 234) to protactinium—234 (atomic number 91, mass number 234):

$$_{90}^{234}\text{Th} \rightarrow {}_{91}^{234}\text{Pa} + {}_{-1}^{0}e$$
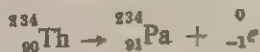
Once again in writing this nuclear reaction we ignore the residual charge on $_{91}^{234}\text{Pa}$.

A point must be understood well that beta particles are not one of the constituents of the nucleus. In some ways, not yet understood fully, a neutron in the nucleus changes to a proton and an electron, which electron is then ejected with a tremendous velocity.

Although beta particles and electrons are identical in their electrical nature and charge/mass ratios, there is a fundamental difference between them. *Ejection of an electron from an atom converts a neutral atom into a positively charged ion but leaves the nucleus undisturbed. Ejection of a beta particle changes the very composition of the nucleus and produces an atom of the next higher atomic number.*

Neutrino: Breaking down of a neutron into a proton and a beta particle creates a problem with the principle of conservation of angular momenta. Particles like neutron, proton and electron have spin angular momentum of $\pm \frac{1}{2} h/2\pi$ each. It is thus seen that the equation:

$$_{0}^{1}n \rightarrow {}_{1}^{1}\text{H} + {}_{-1}^{0}e$$
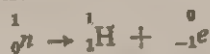
is not balanced insofar as angular momentum is concerned. If the angular momenta of the proton and the electron are $+\frac{1}{2}h/2\pi$ they exceed the angular momentum of the neutron. If they oppose each other then the moment become a zero in violation of that of the neutron. Pauli, therefore, postulated that alongwith the ejected beta particle another tiny neutral particle called neutrino is also ejected. This neutrino has also a spin angular momentum of $\pm \frac{1}{2} h/2\pi$. The sum of the angular momenta of the particles ejected (say $+\frac{1}{2} h/2\pi$ for the proton, $-\frac{1}{2} h/2\pi$ for the electron and $+\frac{1}{2} h/2\pi$ for the neutrino) may now be $+\frac{1}{2}h/2\pi$ being the same as that of the neutron (say $+\frac{1}{2}h/2\pi$). The mass of the neutrino is around 0.00002 with respect to oxygen—16 scale.

12.2.3. Gamma rays: These consist of electromagnetic radiation of very short wave length ($\lambda \sim 0.005-1\text{A}$). These are high energy photons. The emission of gamma rays accompanies all nuclear reactions. During all nuclear reactions there occurs a change in the energy of the nucleus due to emission of alpha or beta particles. The unstable, excited nucleus resulting from the emission of an alpha or beta particle gives off a photon and drops to a lower and more stable energy state. *Gamma rays do not carry charge or mass, and hence emission of these rays cannot change the mass number or atomic number of the mother nucleus.* For simplicity emission of gamma rays is not commonly shown in nuclear reactions.

A perusal of these three types of radiations shows that alpha particles and beta particles are charged species whereas the gamma rays are not. Hence 'in an

electric field or magnetic field the paths of the alpha particles and beta particles are modified whereas the gamma rays pass straight through undeflected. More-

Gamma
Alpha
Beta

M M
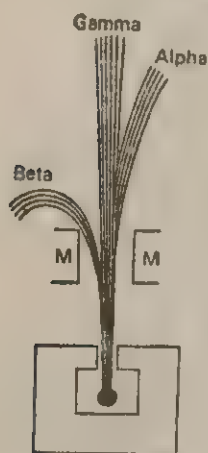
FIG. 12.2. Deflection of radioactive rays in a magnetic field. The sample is enclosed in a lead block

over the alpha particles and the beta particles are deflected towards negative and positive electric terminals respectively or to the two opposite poles of a magnetic field. Besides, the alpha particles being far more massive are deflected to a smaller extent than the beta particles. The relative response to an applied magnetic field is shown schematically in Fig. 12.2. A historical anecdote may be added to this figure. This figure first appeared in the Doctoral dissertation of Marie Curie. More interestingly the announcement of Marie Curie's sharing the 1903 Nobel Prize came the same very year she was admitted to the Doctorate by Sorbonne.

The alpha particles have initial velocities in the range of $1.5-2.0 \times 10^9$ cm/sec, approximately about a tenth of the velocity of light. Since the mass and velocity of the alpha particles are large, they possess great momentum. However they can be stopped by an aluminium foil $\sim 1/10$ mm thick. The absorption of alpha rays by metal foil depends not only on the thickness but also on the atomic weight of the element forming the foil. The alpha particles can travel only a few centimetres of air before losing their energy. While doing so they ionise the air. They can travel no more than $2.8-8.6$ cm of atmospheric air.

The beta rays are ejected with tremendous velocity, being of the order of one-third of that of light. Sometimes the velocity becomes of the order of light. Because of this very high velocity beta rays are far more penetrating than the alpha rays. An aluminium foil about 5 mm thick can stop these rays. The same effect may be achieved by a lead foil only about 1 mm thick, again indicating the effect of the atomic weight of the absorbing material.

Gamma rays are short wave radiations which are not deflected by electric or magnetic fields. They are identical to X-rays but have still shorter wave lengths (X-rays, $\lambda : 10^{-7}$ to 10^{-9} cm; γ rays: λ, 10^{-9} to 10^{-11} cm). These rays possess no mass and hence they are best considered as electromagnetic radiations similar to light. As a result of the very short wave length gamma rays are very penetrating. These may penetrate as much as 25 cm of iron and upto 8 cm of lead.

12.2.4. Positrons : Since the works of the Curies and Rutherford yet another mode of nuclear transformation has been discovered. This involves the ejection of a positron $_{+1}^0e$ from within the nucleus. This ejection is made possible by the conversion of a proton into a neutron.

$$_1^1H \rightarrow {}_0^1n + {}_{+1}^0e$$
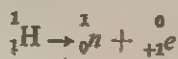
An example is the transformation of $_{51}^{120}Sb$ to $_{50}^{120}Sn$;

$$_{51}^{120}Sb \rightarrow \, _{50}^{120}Sn + \, _{+1}^{0}e$$
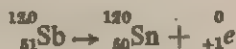
The ejection of positron lowers the atomic number by one unit but leaves the mass number unchanged.

12.3. NUCLEAR REACTIONS VERSUS CHEMICAL REACTIONS

Nuclear reactions are different from chemical reactions in many respects:

1. Chemical reactions involve some loss, gain or overlap of outer orbital electrons of the reactant atoms. Such reactions cannot alter the composition of the nuclei, so that the atomic numbers of the elements remain unchanged. On the contrary nuclear reactions involve emission of alpha particles, beta particles or positrons from inside the nucleus, which leads to a change in the atomic number of the nucleus. In some artificially induced nuclear reactions, neutrons are absorbed by a target nucleus producing an isotope. Nuclear reactions therefore lead either to the birth of another element or produce isotope of the parent element.

2. Nuclear reactions are accompanied by energy changes which far exceeds the energy changes in chemical reactions. For example, the energy evolved in the radioactive transformation of one gram of radium is five hundred thousand times as large as the energy released when one gram of radium combine with chlorine to form $RaCl_2$.

3. The nuclear reactivity of a radioelement is independent of its state of chemical combination. The radium atom in elementary radium and the radium ion in $RaCl_2$ are similar in their radioactive behaviour.

4. In expressing chemical reactions we take into consideration the number of extranuclear electrons that participate in such reactions. In nuclear reactions this is not considered since nuclear reactions take place within the nucleus.

5. Different isotopes of the same element show identical chemical properties since they possess the same electronic configurations. But these isotopes show different nuclear properties. For example, $_{6}^{12}C$ and $_{6}^{14}C$ possess similar chemical properties but their nuclear properties are widely different. $_{6}^{12}C$ is very stable but $_{6}^{14}C$ decays spontaneously by beta emission giving a stable nucleus of $_{7}^{14}N$.

6. Whereas chemical reactions are dependent on external conditions such as temperature and pressure, nuclear reactions are not.

12.4. NUCLEAR INSTABILITY—THE CAUSE OF RADIOACTIVITY

Since radioactivity is a nuclear phenomenon it must be connected with the instability of the nucleus. We have already learnt that the nucleus of an atom is composed of two fundamental particles, protons and neutrons. Since all elements are not radioactive, the ratio of neutron to proton of the unstable, radioactive

nucleus is the factor responsible for radioactivity: Nuclear scientists have studied this problem and have concluded that the stability or the instability is connected with the pairing of nuclear spins. Just as electrons spin around their own axes and just as electron-spin pairing leads to stable chemical bonds, so also the nuclear protons and neutrons spin around their own axes, and pairing of spins of neutrons among neutrons, and pairing of spins of protons among protons lead to nuclear stability. When all the non-radioactive, that is, stable isotopes of the elements are considered it is observed that nuclei with even number of protons and with even number of neutrons are the most abundant. It will be noted that even numbers lead to spin pairing, and odd number leads to unpaired spins. Nuclei with either of the proton number or the neutron number odd are slightly less stable than even numbered ones. By far the least stable isotopes are those which have odd numbers of protons and odd number of neutrons. The nuclear spin pairing is a minimum when odd numbers of both are present.

Alongwith the odd or even number of protons and neutrons, the nuclear stability is also profoundly influenced by the relative numbers of protons and neutrons. The neutron/proton ratio (n/p) helps us to predict which way an unstable radioactive nucleus will decay. A useful graph is obtained by plotting the number of neutrons in the nuclei of the stable isotopes against the respective number of protons. Such a plot is shown in Fig. 12.3. A study of the figure shows that the actual n/p plot of stable isotopes breaks off from the hypothetical 1 : 1 n/p plot at around an atomic number 20, and thereafter rises rather steeply. This indicates that as the number of protons increases inside the nucleus more and more neutrons are needed to minimise the proton-proton repulsion and thereby to add to nuclear stability. Neutrons therefore serve as binding material inside the nucleus.
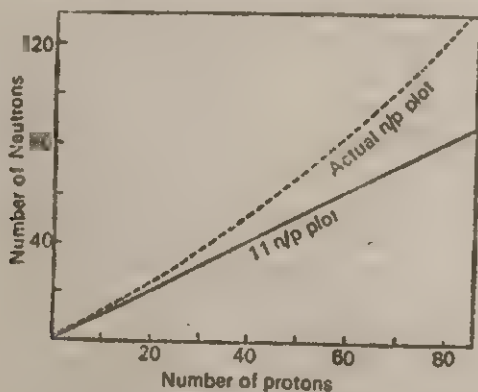
Fig. 12.3. n/p ratio in stable isotopes

The way an unstable nucleus will disintegrate will be decided by its position with respect to the actual n/p plot of stable nuclei. When an isotope is located above this plot it has too high an n/p ratio, and when it is located below the plot it has too low an n/p ratio. In either case the unstable nucleus should decay so as to approach the actual n/p plot. We now discuss the two cases of decay:

12.4.1. Neuron-to-proton ratio too high : An isotope with too many neutrons in the nucleus (that is, with more neutrons than is needed for stability) can attain greater nuclear stability if one of the neutrons decays to a proton. Such a disintegration leads to the ejection of an electron from inside the nucleus:

$$_0^1 n \rightarrow {}_1^1 H + {}_{-1}^0 e$$
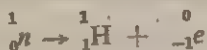
Thus beta ray emission will occur whenever the n/p ratio is higher than the n/p value expected for stability. This is almost always the case when the mass number of the radioactive isotope is greater than the average atomic weight of the element.

The n/p ratio for stable carbon-12 is 1.0 but that of carbon-14 is 1.3. It can be predicted that carbon-14 will be radioactive and will emit beta rays. Similarly the n/p ratio for stable iodine-127 is 1.4. For iodine-133 the n/p ratio equals 1.5 and it is again predicted to be a beta emitter. Experiments reveal that these predictions are correct.

$$_6^{14} C \longrightarrow {}_7^{14} N + {}_{-1}^0 e \; ; \; {}_{53}^{133} I \rightarrow {}_{54}^{133} Xe + {}_{-1}^0 e$$
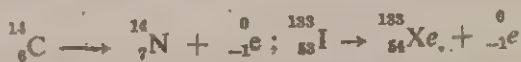
Recall that beta emission increases the atomic number of the daughter by one unit.

12.4.2. Neutron-to-proton ratio too low : A nucleus deficient in neutrons will tend to attain nuclear stability by converting one of its protons to a neutron and this will be achieved either by the emission of a positron or by the capture of an electron. Such decay occurs with a radioactive isotope whose mass number is less than the average atomic weight of the element.'

Positron emission occurs with light isotopes (low n/p) of elements of low atomic number. Thus nitrogen-13 ($n/p = .86$) decays by positron emission. Similarly iodine-121 has an n/p ratio 1.3 which is below the n/p ratio of 1.4 of stable iodine and thus expectedly decays by positron emission.

$$_7^{13} N \longrightarrow {}_6^{13} C + {}_{+1}^0 e \; ; \; {}_{53}^{121} I \longrightarrow {}_{52}^{121} Te + {}_{+1}^0 e$$
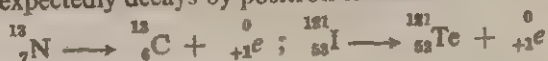
Recall that a positron emission reduces the atomic number by one unit.

Orbital electron capture occurs with too light isotopes (too low n/p) of elements of relatively high atomic number. For such elements the nucleus captures an electron from the nearest orbital (K shell; $n = 1$) and thus changes one of its protons to a neutron. Examples are:

$$_{37}^{82} Rb + {}_{-1}^0 e \longrightarrow {}_{36}^{82} Kr \; ; \; {}_{79}^{194} Au + {}_{-1}^0 e \longrightarrow {}_{78}^{194} Pt$$
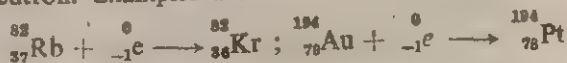
The net effect of the nuclear transformation resulting from orbital electron (K electron) capture is the same as that observed with positron emission. In both cases, a proton in the nucleus is converted to a neutron. In orbital electron capture as soon as the K electron drops into the nucleus electrons move in successively from higher energy orbitals to fill in the vacancy in the K shell. The excess energy in such transitions is given off in the form of X-rays.

The Fig. 12.3 extends to bismuth-209 (atomic number 83) only, since no nucleus heavier than this is known to be stable. Thus we conclude that among the

heaviest nuclei the total proton-proton repulsion is much too large—so large that the binding effect of neutrons is not enough even to lead to a single, stable non-radioactive isotope. For such nuclei alpha particle emission is a common mode of decay. Examples are:

$$_{90}^{232}Th \longrightarrow {}_{88}^{228}Ra + {}_2^4He \; ; \; {}_{92}^{235}U \longrightarrow {}_{90}^{231}Th + {}_2^4He$$

$$_{92}^{238}U \longrightarrow {}_{90}^{234}Th + {}_2^4He$$
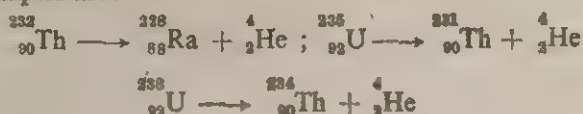
The isotopes $_{88}^{228}Ra$, $_{92}^{231}Th$ and $_{92}^{234}Th$ are not stable either. These too decay till the decay products are isotopes of stable, non-radioactive lead.

12.5. DISINTEGRATION SERIES AND GROUP DISPLACEMENT LAW

We have just seen that the radioactive elements continue to undergo successive disintegration till the daughter elements become stable, non-radioactive isotope of the element lead. The mother element alongwith all the daughter elements down to the stable isotope of lead comprise what is called a radioactive disintegration series. A great deal of physical and chemical investigations was needed to identify the different stages in the disintegration series. One such series is shown in Table 12.1. Uranium-238 decays ultimately to an isotope of lead. The entire route involves alpha emissions in eight stages and beta emissions in six stages, the overall process being:

$$_{92}^{238}U \longrightarrow {}_{82}^{206}Pb + 8 \, {}_2^4He + 6 \, {}_{-1}^0e$$
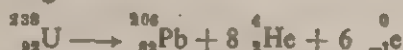
Table 12.1. Uranium-238 Radioactive Disintegration Series (4n + 2 series)
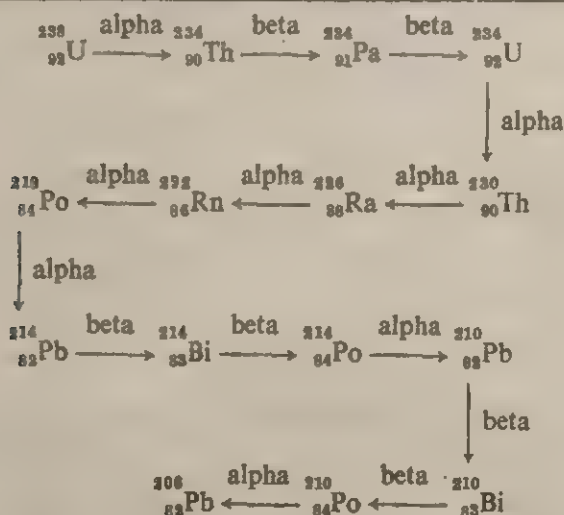
The mass numbers of all the above disintegration products are given by $4n + 2$ ($n = 59$ for uranium-238). This disintegration series is also known as $4n + 2$ series ($n =$ an integer).

The identification of so many steps in the entire course posed a problem with respect to the accommodation of the decaying elements and their daughters in the Periodic Table. It was at this time (1913) that Soddy proposed his group displacement law:

"When an alpha particle is emitted in a radioactive disintegration step, the product is displaced two places to the left in the Periodic Table but the emission of a beta particle results in a displacement of the product to one place to the right." We have already stated this in terms of change in atomic number. A point must be brought home to the young readers: the year when Soddy proposed the law was 1913 and our knowledge of atomic structure was still incomplete. Soddy had to rely on his own chemical intuitions to propose the law. Extensive chemical studies on the disintegration products of the different series preceded the announcement of the law. Soddy also observed that more than one product often belonged to the same Periodic group. He further established that the product elements belonging to the same group positions, had identical chemical properties, though their radioactivities were different. Soddy coined the term *isotope* (same place) for such elements occupying the same place in the Periodic Table. We have already introduced the term 'isotope' in Chapter 1 and have seen that varying number of neutrons in the nucleus of atoms of the same element are responsible for the different atomic weights of the isotopes. A study of the displacement law further reveals that when a parent radioelement emits one alpha particle, the daughter a beta particle and its daughter again a beta particle, then the product occupies the same Periodic group as the parent radioelement.

The radioactive series shown in Table 12.1 was the first to be disovered. Two other series were discovered later: the $4n + 3$ series (n = an integer) starts with uranium-235 and ends with the stable isotope lead-207 and the $4n$ (n = an integer) series starts with thorium-232 and ends up in lead-208.

Table 12.2. Uranium-235 Disintegration Series ($4n + 3$ series)

$$^{235}_{92}U \xrightarrow{\text{alpha}} {}^{231}_{90}Th \xrightarrow{\text{beta}} {}^{231}_{91}Pa \xrightarrow{\text{alpha}} {}^{227}_{89}Ac$$

$$\downarrow \text{beta}$$

$$^{215}_{84}Po \xleftarrow{\text{alpha}} {}^{219}_{86}Rn \xleftarrow{\text{alpha}} {}^{223}_{88}Ra \xleftarrow{\text{alpha}} {}^{227}_{90}Th$$

$$\downarrow \text{alpha}$$

$$^{211}_{82}Pb \xrightarrow{\text{beta}} {}^{211}_{83}Bi \xrightarrow{\text{alpha}} {}^{207}_{81}Tl \xrightarrow{\text{beta}} {}^{207}_{82}Pb$$
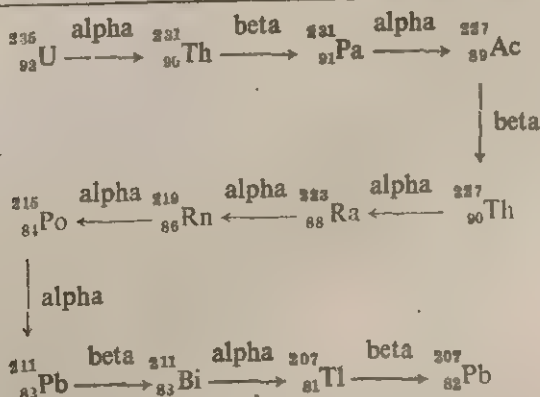
Table 12.3. Thorium-232 Disintegration Series (4n series)

$$^{232}_{90}Th \xrightarrow{\text{alpha}} {}^{228}_{88}Ra \xrightarrow{\text{beta}} {}^{228}_{89}Ac \xrightarrow{\text{beta}} {}^{228}_{90}Th$$

$$\downarrow \text{alpha}$$

$$^{212}_{82}Pb \xleftarrow{\text{alpha}} {}^{216}_{84}Po \xleftarrow{\text{alpha}} {}^{220}_{86}Rn \xleftarrow{\text{alpha}} {}^{224}_{88}Ra$$

$$\downarrow \text{beta}$$

$$^{212}_{83}Bi \xrightarrow{\text{beta}} {}^{212}_{84}Po \xrightarrow{\text{alpha}} {}^{208}_{82}Pb$$
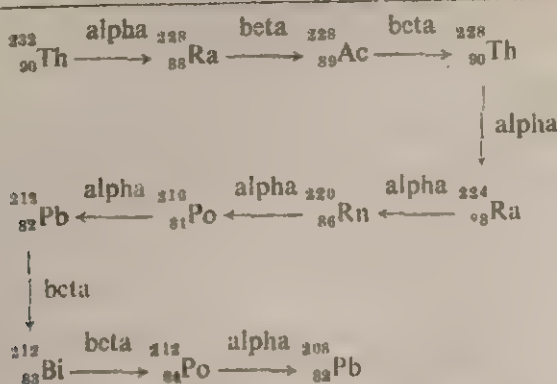
The reader should note that all three radioactive series end in lead. This is because of the fact that all the three isotopes of lead $\left({}^{206}_{82}Pb, \; {}^{207}_{82}Pb, \; {}^{208}_{82}Pb\right)$ are non-radioactive and furthermore lead is nearest to the naturally occurring radio-elements.

12.6. MEASUREMENTS OF RADIOACTIVITY

Measurements of radioactivity are based on the following principles: (a) radioactive radiations can ionise a gas, (b) radioactive radiations can produce luminiscence in substances like zinc sulphide or barium platinocyanide, (c) radioactive radiations can affect photographic emulsions like ordinary light rays.

(a) A charged particle like an alpha or beta particle is endowed with a strong electric field all around itself. Such particles, while moving through a gas, can lead to ejection of orbital electrons from the atoms or molecules constituting the gas. Thus the passage of charged particles result in the formation of ion-pairs—orbital electrons and the resulting positive ions. The more slowly moving particle spends more time in the vicinity of the gaseous atoms or molecules, and hence it creates more ion-pairs. Gamma rays also indirectly eject electrons with great velocity. These fast moving electrons in their turn again produce ion-pairs.

During the early days of radioactivity Becquerel and Curies made use of a gold leaf electroscope for measurements of radioactivity. These measurements were made possible because of the ionisation of the air by the radiations. A gold leaf electroscope (Fig. 12.4) consists of a short vertical metal rod with a metal plate at the top. At the lower end of the metal rod are attached two small rectangular gold leaves, hanging vertically. A major portion of the rod alongwith the declicate gold leaves is enclosed in a box. Proper

Charged   Discharged

FIG. 12.4. Gold leaf electroscope

insulation is made and the arrangement protects the gold leaves from air currents. If an electric charge is applied to the top metal plate, the gold leaves repel each other due to accumulation of similar charge. If the air in the box is now ionised due to alpha, beta or gamma rays, then the air becomes an electrical conductor and allows the gold leaves to be discharged. The charge on the leaves passes into the air, repulsion of the leaves ceases and the leaves come back to the vertical positions. Becquerel found that a uranium salt brought close to a charged electroscope caused the latter to discharge.

Modern equipments for measurements of radioactivity also utilise the ionisation principle. The ionisation is amplified into an electrical signal. A common type of Geiger-Muller counter (Fig. 12.5) consists of a metal cylinder through which passes a central wire. The cylinder serves as the cathode and the central wire as the anode. The anode and the cathode are properly insulated. The cylinder
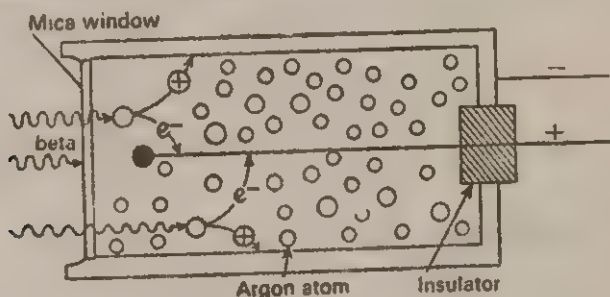
FIG. 12.5. A model of Geiger-Muller tube

has a mica window and is filled with argon gas. A very high voltage (~ 1000 volts) is maintained between the two electrodes. When a radiation (say a beta particle) penetrates the thin mica window and enters the tube, it ionises a large number of argon atoms. Resulting electrons are attracted to the anode wire and the argon cations to the cathode. The tube is thus discharged and current flows. Each discharge is amplified and registered as a loud click or as a number in a suitable counting rate meter.

(b) Becquerel first noted that radioactive radiations, like cathode rays and X-rays, can produce luminiscence in a number of substances such as zinc sulphide or barium platinocyanide. This property of radioactive rays was most prominent with alpha particles. The impact of alpha particles on a screen of zinc sulphide was registered as a bright flash which could be watched in a dark room with a telescope. Counting the number of such flashes provide a quantitative measurement of the radiation. The number of scintillations produced by an alpha ray source on a zinc sulphide screen compares with the results from Geiger-Muller counter. The scintillation technique was abundantly used by Rutherford during the early days of radioactivity.

(c) That radioactive radiations can affect photographic plates formed the very basis of the discovery of radioactivity.

In practice radioactivity is expressed in terms of the number of disintegra-

tions per second. One gram of radium undergoes about 3.7×10^{10} disintegrations per second. The quantity of 3.7×10^{10} disintegrations per second. is called the *curie*, which is the unit of radioactivity. *Millicurie* and *microcurie* respectively correspond to 3.7×10^7 and 3.7×10^4 disintegrations per second. On this basis, radioactivity of radium is 1 curie per gram. Phosphorus-32, a beta-emitter, has an activity of 50 millicuries per gram. This means that for every gram of phosphorus-32 in some material containing this species there are $50 \times 3.7 \times 10^7$ disintegrations taking place per second. One disintegration per second is called a *becquerel*. Thus one *curie* is equivalent to 3.7×10^{10} becquerel.

Neutrons are also involved in many nuclear reactions. Secondary reactions whereby a neutron produces a charged particle like proton or alpha particle via reaction with a suitable compound are made use of in neutron determination. Usually a counter containing BF_3 gas is used. Alternatively the wall of the counter is coated with $BF_3.CaF_2$. As neutrons enter the chamber they force a reaction of the type:

$$^{10}_{5}B + ^{1}_{0}n \rightarrow ^{7}_{3}Li + ^{4}_{2}He$$

The alpha particle then ionises the gas (say argon) inside the chamber and the number of counts recorded gives the number of neutrons.

12.7. RATE OF RADIOACTIVE DECAY

The rate at which a radioactive sample disintegrates can be determined by counting the number of particles emitted in a given time. In such measurements care is exercised to exclude the radioactivity arising out of the disintegration of the daughter element.

Radioactive decay is one important natural phenomenon obeying the first order rate process. The rate can be expressed as:

$$\frac{dN}{dt} = -kN \qquad \qquad \dots (1)$$

where N is the number of the atoms of the disintegrating radioelement, t is the time over which the disintegration is measured and k is the radioactive decay rate constant. k is a specific characteristic of a radioelement. The quantity dN/N represents the fraction of the total number of atoms which disintegrates in time dt. Then $(-dN/N)/dt$ $(= k)$ represents the fraction of radioactive atoms that disintegrates in unit time. dN/dt is the instantaneous rate at which the radioelement disappears. The negative sign shows that N decreases with time. Rearranging and integrating over the limits N_0 and N and time, t and 0:

$$\frac{dN}{N} = -kdt \; ; \quad \int_{N_0}^{N}\frac{dN}{N} = -\int_{0}^{t} kdt \qquad \qquad \dots (2)$$

$$\text{Therefore } \int_{N_0}^{N} d(\ln N) = -\int_{0}^{t} kdt \qquad \qquad \dots (3)$$

$$\ln \frac{N}{N_0} = - kt \quad \text{or} \quad \frac{N}{N_0} = e^{-kt} \qquad \qquad \ldots (4)$$

Converting to the logarithm to the base 10, we have

$$2.303 \log \frac{N_0}{N} = kt \qquad \qquad \ldots (5)$$

If the rate of disappearance of the disintegrating element is followed over a period of time the rate constant k can be evaluated from a plot of $\log \frac{N}{N_0}$ against time t. After a certain period of time the value of $\frac{N}{N_0}$ becomes one-half, that is, half of the radioactive elements have undergone disintegration. This period is called the half life of the radioactive element and is a characteristic property of a radioactive element. The half life is given by

$$2.303 \log (1/\tfrac{1}{2}) = kt_{\frac{1}{2}} \quad \text{so that} \quad t_{\frac{1}{2}} = \frac{0.693}{k} \qquad \qquad \ldots (6)$$

$^{213}_{84}\text{Po}$ has $t_{\frac{1}{2}}$ equal to 4.2×10^{-6} sec, whereas that of $^{209}_{83}\text{Bi}$ is 3×10^7 years. Uranium-238 has a half-life of 4.5×10^9 years.

Radioactive decay measurements allow an accurate determination of the Avogadro number. We have just seen that kN represents the rate of decay of the radioactive element. If N stands for the number of atoms present in one gram of the element then

$$N = \frac{\text{Avogadro number}}{\text{mass number}}$$

Therefore
$$kN = \frac{k. \text{Avogadro number}}{\text{mass number}}$$

$$= \frac{0.693 \times \text{Avogadro number}}{t_{\frac{1}{2}} \times \text{mass number}}$$

If each atom of the radioelement expels one particle then kN, the rate of decay, is also the rate at which such particles are ejected. One gram of radium undergoes 3.7×10^{10} disintegrations per second so that the Avogadro number can be calculated.

$$\text{Avogadro Number} = \frac{3.7 \times 10^{10} \times 1590 \times 365 \times 24 \times 60 \times 60 \text{ second} \times 226}{1 \text{ second} \times 0.693}$$

$$\text{(mass number of radium} = 226$$
$$= 6.0 \times 10^{23} \qquad \qquad t_{\frac{1}{2}} = 1590 \text{ years)}$$

Besides half life of a radioelement, another aspect of the life of a radioelement must also be known. It is possible to determine from the above the average life period of a radioactive atom present in an aggregate of a large number of atoms. Average life period of an atom of the radioelement tells us the average span of

20

time after which the atom will disintegrate. The exponential law of radioactive decay

$$\frac{N}{N_0} = e^{-kt} \; ; \; N = N_0 e^{-kt} \qquad \qquad \dots (7)$$

indicates that there is a certain probability that a particular atom will disintegrate at a given time. The law also shows that the probability is proportional to the number of atoms present at that given time. The length of time a radioelement atom can live before it disintegrates may have values from zero to infinity. This explains the gradual decay of the radioelement instead of a decay of all the atoms at the same time. The equations (1) and (7) can be rearranged to give:

$$dN = -kNdt = -kN_0 e^{-kt} dt \qquad \qquad \dots (8)$$

In the small time interval dt (between t and $t + dt$) a small number of atoms dN disintegrate. Since dt is a small time period we can take dN as the number of atoms disintegrating at the time t. If we start recording time t from a particular instant, then dN represents the number of atoms with a life span of t. The total number of atoms N_0 is composed of many such small numbers of atoms dN_1, dN_2, dN_3, etc. each with its own life span t_1, t_2, t_3, etc. The life span t will vary from zero to infinity due to the exponential nature of the decay.

The sum of the products of the type tdN divided by the total number of atoms N_0 will give the average life of the radioelement.

$$t_{av} = \frac{t_1 dN_1 + t_2 dN_2 + t_3 dN_3 + \dots}{N_0} = \int_0^\infty \frac{tdN}{N_0}$$

$$= -\int_0^\infty \frac{tkNdt}{N_0} = -\int_0^\infty \frac{tkN_0 e^{-kt} dt}{N_0} = -\int_0^\infty tke^{-kt} dt$$

$$= -\left[\frac{kt+1}{k} e^{-kt} \right]_0^\infty = \frac{1}{k}$$

The average life of a radioelement is thus the reciprocal of its radioactive disintegration constant. This result can also be derived in a very simple, alternatve way. Since the radioactive atoms may be regarded as having an average life, then the product of the fractions of atoms disintegrating in unit time (that is k) and average life must be unity.

$$t_{av}k = 1 \text{ so that } t_{av} = \frac{1}{k}$$

The connection between average life and half life is thus simple:

$$t_{\frac{1}{2}} = \frac{0.693}{k} = 0.693 t_{av}$$

It is obvious that a short lived radioelement has small value for its $t_{\frac{1}{2}}$ and t_{av}, and very high value of decay constant. It should be noted, however, that a definite fraction k will decay in unit time, although we cannot forecast which particular atoms will disintegrate.

Some important aspects of radioactive disintegration process need to be noted.

1. Since the disintegration process obeys the first order rate law, the $t_\frac{1}{2}$ is independent of the amount of the sample. Another way of stating this is that the rate (not rate constant k) at which the disintegration occurs is proportional to the amount of the element present. The independence of $t_\frac{1}{2}$ of the amount of the sample is shown by decay curve of iodine-131 (Fig. 12.6)—a beta emitter with half life of 8.1 days.

2. The rate of decay is independent of pressure and temperature. It implies that the activation energy for radioactive decay is zero.

3. After n half lives have elapsed the amount of the radioactive element remaining will be $(\frac{1}{2})^n$. For example, after four half lives only 1/16th of the orginal element will be left behind.
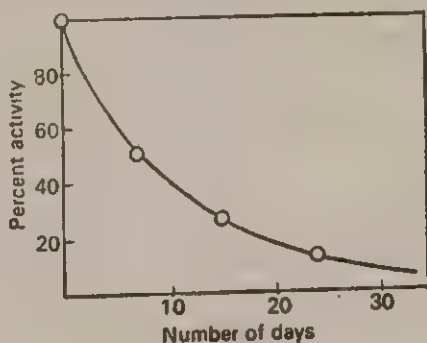
FIG. 12.6. Decay curve of iodine-131

Problem: Half life of Rn-222 is 3.82 days. Calculate the weight of 1 *curie* of Rn-222.

1 *curie* of Rn-222 is that weight which produces 3.7×10^{10} disintegrations per sec.

$$k = \frac{0.693}{t_\frac{1}{2}} = \frac{0.693}{3.82 \times 24 \times 60 \times 60} \text{ sec}^{-1} = 2.1 \times 10^{-6} \text{ sec}^{-1}$$

Given $-\frac{dN}{dt} = 1$ curie $= 3.7 \times 10^{10}$ disintegrations sec^{-1}

Let x be the required weight of Rn-222 in gm.

$$-\frac{dN}{dt} = kN = k\frac{x}{222} \times 6.02 \times 10^{23} = 3.7 \times 10^{10}$$

Here $\frac{x}{222} \times 6.02 \times 10^{23}$ represents the number of atoms of Rn-222 that will produce 1 *curie* disintegrations.

$$\therefore x = 6.5 \times 10^{-6} \text{ gm.}$$

Problem: 1.00 gm pitchblende contains 70 per cent uranium. Assuming that there has been no loss of radon gas from the ore how many alpha emissions and how many beta emissions will occur per second ? ($t_{\frac{1}{2}}$ for uranium-238 is 4.5×10^9 years).

Table 12.1 shows that uranium-238 series gives a total of eight alpha particles and six beta particles for every U-238 atom. The problem is to find first the number of U-238 atoms that disintegrate per second.

$$k = \frac{0.693}{4.5 \times 10^9 \times 365 \times 24 \times 60 \times 60 \text{ sec}}$$

$$\therefore -\frac{dN}{dt} = kN = \frac{0.693}{4.5 \times 10^9 \times 365 \times 24 \times 60 \times 60 \text{ sec}} \times \frac{0.7 \times 6.02 \times 10^{23}}{238}$$

$$= 0.868 \times 10^4 \text{ sec}^{-1} \text{ (1 gm pitchblende contains 0.7 gm U-238)}$$

$\therefore$ number of alpha emissions per second

$$= 0.868 \times 10^4 \times 8 \text{ sec}^{-1} = 69240 \text{ sec}^{-1}$$

$\therefore$ number of beta emissions per second

$$= 0.868 \times 10^4 \times 6 \text{ sec}^{-1} = 52100 \text{ sec}^{-1}$$

Problem: 1 gm radium-226 is placed in a sealed tube. How much helium will be evolved in 60 days ? ($t_{\frac{1}{2}} = 1590$ years).

From Table 12.1 it is seen that each radium-226 gives out five alpha particles.

$$k = \frac{0.693}{1590 \times 365 \text{ days}}$$

$$\therefore -\frac{dN}{dt} = kN = \frac{0.693 \times 1 \times 6.02 \times 10^{23}}{1590 \times 365 \text{ days} \times 226} = 3.18 \times 10^{15} \text{ per day}$$

So the number of radium-226 atoms disintegrating in 60 days $= 60 \times 3.18 \times 10^{15}$.

Number of alpha particles produced $= 5 \times 60 \times 3.18 \times 10^{15}$. Avogadro number of helium atoms occupy 22.4×10^3 ml at N.T.P. Thus the volume of helium gas is given by:

$$\frac{5 \times 60 \times 3.18 \times 10^{15} \times 22.4 \times 10^3}{6.02 \times 10^{23}} = 0.035 \text{ ml.}$$

Problem: 2.00 g of $_{83}^{210}Bi$ decays at such a rate that 0.500 gm of it is left after 10 days. Calculate (a) the radioactive decay rate constant k (b) the amount left after five days and (c) the half life of the isotope.

(a) $2.303 \log \frac{N_0}{N} = kt$

Then $kt = 2.303 \log (2.00/0.50) = 2.303 \log 4.00$

$\therefore k = 2.303 \log 4.00/10 \text{ days} = 0.138 \text{ day}^{-1}$

(b) $2.303 \log \dfrac{2.00}{N} = 0.138 \,(\text{day})^{-1} \times 5 \,(\text{days})^1 = 0.69$

$\therefore \ \log (2.00/N) = 0.69/2.303 = 0.3$

$\therefore \ \log N = \log 2.00 - 0.3 = 0$

$\therefore \ N = \text{antilog of } 0 = 1.00 \text{ g.}$

(c) half life is given by $2.303 \log (1/\tfrac{1}{2}) = kt_{\frac{1}{2}}$

$\therefore \ t_{\frac{1}{2}} = \dfrac{0.693}{k} = \dfrac{0.693}{0.138 \,(\text{day})^{-1}} = 5 \text{ days}$

12.8. RADIOACTIVE EQUILIBRIUM

The rate at which a radioelement decays must also be the rate at which the daughter element is formed. If these radioelements are members of a disintegration series then the above daughter must again decay to produce its own daughter and so on. Since the rate of decay of a mother element is equal to the rate of formation of its daughter, and also since rate of decay is dependent on the amount of each element, it follows that a state of equilibrium will soon be reached. Thus

$$\frac{dN_1}{dt} = \frac{dN_2}{dt} = \frac{dN_3}{dt} \text{ etc.}$$

where N_1, N_2, N_3, etc. represent the number of atoms of the different radioelements in the series present at equilibrium. It follows from equation (I) of the preceding section that

$$k_1 N_1 = k_2 N_2 = k_3 N_3$$

At radioactive equilibrium the amounts of radioelements are therefore inversely proportional to their decay rate constants. Recall that half life $t_{\frac{1}{2}}$, and k have an inverse relation. Therefore the amounts of radioelements in a decay series are directly proportional to their respective half life periods.

An important aspect of radioactive equilibrium is that even though different amounts of radioelements are present, all elements at equilibrium disintegrate at the same rate. Same number of atoms of different elements disintegrate in a given time. This becomes obvious from the above relations.

Radioactive equilibrium is conceptually very different from chemical equilibrium. A chemical equilibrium is established when the rates of the forward reaction and the backward reaction are the same. Such an equilibrium is reversible and may be made to go this way or that by a change in temperature, pressure or concentration of the species involved. A radioactive equilibrium is irreversible and no change in the external conditions can bring about a change in the equilibrium.

12.9. ARTIFICIAL TRANSMUTATION

Having described his brilliant experiments on alpha particle scattering by thin metal foils of platinum, gold, etc. in 1909, Rutherford started probing with his alpha particles in still newer areas. These ventures paid off, and Rutherford

announced yet another startling discovery of synthesizing elements by artificial means.

Rutherford reported in 1919 that high energy alpha particles interact with nitrogen gas to produce protons of high energy and hence of longer penetrating range. Rutherford made sure that the protons had not arisen out of impurity in the nitrogen. Control experiments done on very pure hydrogen showed that the protons resulting from ionisation by alpha particles were far less energetic, hence of shorter range. Rutherford succeeded in proving that this bombardment of nitrogen by fast moving alpha particles had led to a nuclear reaction of the type:

$$\ _{7}^{14}N + \ _{2}^{4}He \rightarrow \ _{8}^{17}O + \ _{1}^{1}H$$

The reaction has given birth to an isotope of oxygen. This was the first example of artificial transmutation of elements. Thus Rutherford made a small but sure step to the realisation of alchemists' dream of turning iron into gold. Syntheses of hitherto unknown elements became possible in course of time.

On account of the very high repulsion between positively charged alpha particle and a heavy atom nucleus (say of gold, platinum, etc.) of high positive charge, no artificial transmutation could be achieved by Rutherford; instead these experiments provided us with one of the most important clues to the atomic structure (Chapter 1).

Later experiments by Chadwick showed that other elements could be built from lighter elements. When powdered beryllium is mixed with a trace of the alpha emitter radium, the following reaction occurs:

$$\ _{4}^{9}Be + \ _{2}^{4}He \rightarrow \ _{6}^{12}C + \ _{0}^{1}n$$

Incidentally it may be mentioned that this particular transmutation reaction led to the discovery of neutron.

These discoveries inspired nuclear scientists to undertake many different types of artificial transmutation reactions. Other bombarding projectiles were soon tried and new results obtained. Techniques were also devised to increase the speed of the bombarding projectiles so that the projectiles could effectively hit the target and bring about a nuclear reaction.

It is believed that at first an *unstable compound nucleus* is formed out of the reaction of the target nucleus and the bombarding particle. The compound nucleus then emits one or more particles of high energy and changes to a new nucleus in order to gain stability. A positively charged projectile (say, a proton) will naturally be strongly repelled by the positive field of the target nucleus. This repulsive barrier is usually overcome by imparting enhanced speed to the projectile. A neutron (being devoid of a charge) has no repulsive barrier and thus nuclear transmutations are more easily achieved with neutrons. Examples of some artificial transmutations are given in Table 12.4. High energy gamma radiation has also been found to result in transmutation of the (γ, n) type:

$$\ _{1}^{2}D + \gamma \longrightarrow \ _{1}^{1}H + \ _{0}^{1}n; \ _{4}^{9}Be + \gamma \rightarrow \ _{4}^{8}Be + \ _{0}^{1}n$$
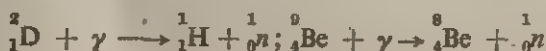
These gamma-radiation (photo-) induced reactions have been variously termed as *photodisintegration*, *photonuclear reaction* or as *nuclear photoeffect*.

Table 12.4. Typical Bombardment (Transmutation) Reactions

Bombarding particle	Expelled particle	Transmutation Reactions	
Proton	^1_0n	$^{31}_{15}P + ^1_1H \longrightarrow ^{32}_{16}S + ^1_0n$	(p, n) (p)
	^4_2He	$^{11}_5B + ^1_1H \longrightarrow 3\,^4_2He$	
		$^{14}_7N + ^1_1H \longrightarrow ^{11}_6C + ^4_2He$	(P, α)
		$^{13}_6C + ^1_1H \longrightarrow ^{13}_7N + \gamma$	(P, γ)
Deuteron	^1_1H	$^{75}_{33}As + ^2_1H \longrightarrow ^{76}_{33}As + ^1_1H$	(D, p)
	^1_0n	$^9_4Be + ^2_1H \longrightarrow ^{10}_5B + ^1_0n + \gamma$	(D, n, γ)
	^4_2He	$^{12}_6C + ^2_1H \longrightarrow ^{10}_5B + ^4_2He$	(D, α)
Alpha	^1_0n	$^{27}_{13}Al + ^4_2He \longrightarrow ^{30}_{15}P + ^1_0n$	(α, n)
	^1_1H	$^{19}_9F + ^4_2He \longrightarrow ^{22}_{10}Ne + ^1_1H$	(α, p)
Neutron	^1_1H	$^{27}_{13}Al + ^1_0n \longrightarrow ^{27}_{12}Mg + ^1_1H$	(n, p)
	^4_2He	$^{14}_7N + ^1_0n \longrightarrow ^{11}_5B + ^4_2He$	(n, α)
	$2\,^1_0n$	$^{13}_6C + ^1_0n \longrightarrow ^{11}_6C + 2\,^1_0n$	(n, 2n)
		$^{238}_{92}U + ^1_0n \longrightarrow ^{237}_{92}U + 2\,^1_0n$	(n, 2n)
	γ	$^1_1H + ^1_0n \longrightarrow ^2_1H + \gamma$	(n, γ)

The Cyclotron: It is a machine used to impart extra kinetic energy to posi-

tively charged projectiles. Charged particles are accelerated by the simultaneous, application of an electric and magnetic field.

The cyclotron consists of two D-shaped semicircular hollow boxes (D_1 and D_2) known as *dees*. The two *dees* are a few cm apart and are placed in a closed vessel. At the centre S of the corridor between the two dees there is an electrically heated filament which emits electrons (thermionic emission). The dees alongwith the enclosing vessel is placed between the poles of a powerful electromagnet. The dees are connected to an alternating high voltage source.

The vessel is evacuated and an appropriate gas (hydrogen, deuterium or helium) is introduced. The electron beam from the heated filament ionises the gas at S and thus positive projectiles (proton, deuteron or alpha particle as the case may be) are generated.

Fig. 12.7. Working principle of a cyclotron: (a) oscillating high voltage (b) high energy beam. Large evacuated chamber encloses the dees.

Let us assume that at a particular instant D_2 is negative. The positive ion at S will then move towards D_2 but then it is also under the influence of a magnetic field at right angles to the electric field. The result is that it moves in a circular path inside D_2. As it emerges from D_2 and reaches the corridor between the dees it is again under the influence of the applied potential difference. If the oscillating high voltage source changes its sign at the moment the positive ion reaches the corridor then D_1 will be negative and the positive ion will be accelerated towards D_1. Since its energy is now greater it will move faster. With increase in velocity the radius of curvature of its path will also increase. It follows (page 6):

$$\frac{e}{m} = \frac{v}{Hr} \; ; \; r = \frac{vm}{eH}$$

where m is the mass of the ion, e is the charge, v the velocity, H the magnetic field and r the radius of curvature of the circular path. So m, e and H remaining constant, r has to increase with increasing velocity.

If the above movement is repeated over and over again the particles will move faster and faster in paths of larger and larger radius. Finally these are deflected from the periphery of one of the dees and are made to strike the target.

A very novel feature of the cyclotron is that the time taken by the charged particle in traversing in semicircular path in the dees is independent of both the velocity of the particle and the radius of the path. Since a dee is half a circle the length of the path is πr, so that time t taken by the particle to complete traversing πr is:

$$t = \frac{\pi r}{v} = \frac{\pi m}{He}$$

which carries neither v nor r. Thus increased length due to increased r is balanced by increased v.

12.10. ARTIFICAL RADIOACTIVITY

In the early thirties Irene and Frederick Joliot-Curie devoted themselves to the study of artificial transmutation reactions. By bombarding certain light isotopes with alpha particles, they produced several isotopes of low mass numbers. Some of the reactions provided interesting results. Aluminium target was bombarded by alpha particles with the following results:

$$^{27}_{13}Al + {}^4_2He \rightarrow {}^{30}_{15}P + {}^1_0n$$
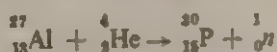
The Joliot-Curies noted with happy anguish that the reaction was accompanied with positron emission, and further that on withdrawing the alpha particle source neutron emission stopped but not that of positron. This could be explained only on the basis that the artificially synthesized phosphorus-30 isotope was radioactive and that it decayed by positron emission. It may be noted that non-radio-

$$^{30}_{15}P \rightarrow {}^{30}_{14}Si + {}^0_{+1}e$$
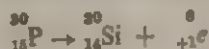
active, naturally occurring phosphorus-31 has 15 protons and 16 neutrons. Hence phosphorus-30 has a low neutron to proton ratio and is apt to decay by positron emission producing stable, non-radioactive silicon-30. Thus the Joliot-Curies were the people to show that radioactivity can also be created artificially by transmutation reactions. Some examples are:

$$^{24}_{12}Mg + {}^4_2He \rightarrow {}^{27}_{14}Si + {}^1_0n; \quad {}^{27}_{14}Si \rightarrow {}^{27}_{13}Al + {}^0_{+1}e$$

$$^{10}_5B + {}^4_2He \rightarrow {}^{13}_7N + {}^1_0n; \quad {}^{13}_7N \rightarrow {}^{13}_6C + {}^0_{+1}e$$
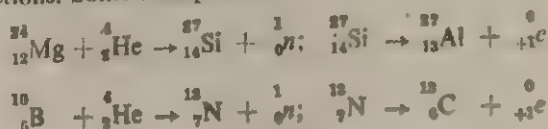
Besides alpha particles, other projectiles can also lead to the syntheses of unstable, radioactive isotopes. Some examples are given below:

$$^{23}_{11}Na + {}^2_1H \rightarrow {}^1_1H + {}^{24}_{11}Na; \quad {}^{24}_{11}Na \rightarrow {}^{24}_{12}Mg + {}^0_{-1}e$$

$$^{32}_{16}S + {}^2_1H \rightarrow {}^{30}_{15}P + {}^4_2He; \quad {}^{30}_{15}P \rightarrow {}^{30}_{14}Si + {}^0_{+1}e$$

$$^{27}_{13}Al + {}^1_0n \rightarrow {}^{24}_{11}Na + {}^4_2He; \quad {}^{24}_{11}Na \rightarrow {}^{24}_{12}Mg + {}^0_{-1}e$$

$$^{39}_{19}K + {}^1_0n \rightarrow {}^{38}_{19}K + 2\,{}^1_0n; \quad {}^{38}_{19}K \rightarrow {}^{38}_{18}A + {}^0_{+1}e$$

$$^{23}_{11}Na + {}^1_0n \rightarrow {}^{22}_{10}Ne + {}^1_1H; \quad {}^{22}_{10}Ne \rightarrow {}^{22}_{11}Na + {}^0_{-1}e$$
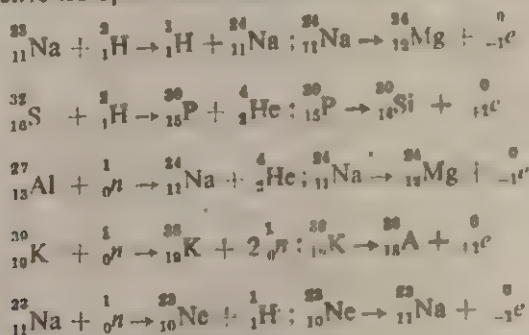
An interesting historical anecdote may be added to the Joliot-Curies' researches on artificial radioactivity. They were at considerable pains with the aluminium—alpha particle reaction because the neutron was not identified and announced at the time they began these researches. In 1932 Chadwick announced the discovery of the neutron as a result of artificial transmutation reaction of

beryllium with alpha particle producing carbon nucleus and neutron. After this announcement the Joliot-Curies realised that their experimental results on the properties of the expelled particle (that is, neutron) coincided with those reported by Chadwick for neutron. Unfortunately the Joliot-Curies missed Rutherford's 1920 Bakerian lecture wherein he predicted the existence of a particle like neutron. If this theoretical clue were known to them, probably the honour of discovering the neutron would have gone to the Joliot-Curies rather than to Chadwick.

Irene and Frederick Joliot-Curie joined the select band of Nobel Laureates in 1934 for their original studies of artificial radioactivity.

12.11. THE MAN-MADE ELEMENTS

Till the year 1937 our Periodic Table ended in uranium (atomic number 92). The Table also had four gaps for four missing elements corresponding to the atomic numbers 43, 61, 85 and 87. Within a span of five years, between 1937 and 1942, radioactive isotopes of these elements (technetium Tc, atomic number 43; promethium Pm, 61; astatine At, 85 and francium Fr, 87) were all synthesized by artificial transmutation techniques:

1. $\quad {}_{42}^{98}Mo + {}_{0}^{1}n \rightarrow {}_{42}^{99}Mo + \gamma \; ; \; {}_{42}^{99}Mo \rightarrow {}_{43}^{99}Tc + {}_{-1}^{0}e$

2. $\quad {}_{60}^{146}Nd + {}_{1}^{1}H \rightarrow {}_{61}^{146}Pm + {}_{0}^{1}n \; ; \; {}_{60}^{147}Nd \rightarrow {}_{61}^{147}Pm + {}_{-1}^{0}e$

3. $\quad {}_{88}^{226}Ra + {}_{0}^{1}n \rightarrow {}_{88}^{227}Ra + \gamma \; ; \; {}_{88}^{227}Ra \rightarrow {}_{89}^{227}Ac + {}_{-1}^{0}e \; ;$

$$ {}_{89}^{227}Ac \xrightarrow{99\%} {}_{90}^{227}Th + {}_{-1}^{0}e $$
$$ \xrightarrow[1\%]{} {}_{87}^{223}Fr + {}_{2}^{4}He $$

4. $\quad {}_{83}^{209}Bi + {}_{2}^{4}He \rightarrow {}_{85}^{211}At + 2\,{}_{0}^{1}n$
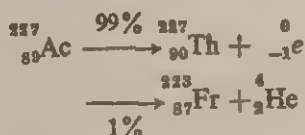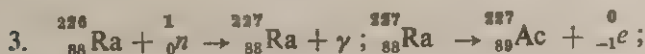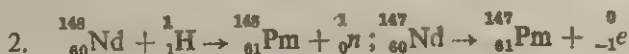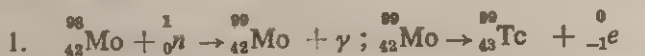
Actinium-227 exhibits a branched disintegration. Besides undergoing a beta decay, it also simultaneously emits an alpha particle. This latter disintegration produces francium-223. Physical and chemical studies identified these elements and assigned to them proper positions in the Periodic Table: francium with the alkalies in group IA, technetium after manganese in group VIIA, astatine with the halogens in group VIIB and promethium with the rare earths.

Twelve more new elements past uranium have now been synthesized and characterised largely through the remarkable efforts of Seaborg at Berkeley, U.S.A. Table 12.5 describes the transmutation reactions performed for these syntheses. Their syntheses and characterisations demanded of the scientists skill, devotion and originality of the highest order. It is interesting to note that these elements have often been obtained in submicrogram ($\sim 10^{-5}$ to 10^{-6} gm) quantities and often with extreme radioactivity. They posed problems of handling, and of physical

and chemical analyses, in submicrogram quantities. Fortunately these analytical obstacles were overcome. Both physical and chemical evidences indicate that these trans-uranium elements are filling up a second series of inner transition elements. Hence in conformity with the lanthanides these elements are called actinides, and they are allotted a single place in group III alongwith actinium (atomic number 89).

The isotopes of the synthetic elements have been obtained in more than one way by changing the target element and the bombarding projectile. Table 12.5 describes but one nuclear reaction for each of these synthetic elements.

Table 12.5. Syntheses of the Actinide Elements

Target		Projectile		Products	
${}^{238}_{92}U$	$+$	${}^{2}_{1}H$	$\rightarrow$	${}^{238}_{93}Np$ (neptunium)	$+\ 2\,{}^{1}_{0}n$
${}^{238}_{92}U$	$+$	${}^{4}_{2}He$	$\rightarrow$	${}^{240}_{94}Pu$ (plutonium)	$+\ 2\,{}^{1}_{0}n$
${}^{239}_{94}Pu$	$+$	${}^{4}_{2}He$	$\rightarrow$	${}^{241}_{95}Am$ (americium)	$+\ {}^{1}_{1}H + {}^{1}_{0}n$
${}^{239}_{94}Pu$	$+$	${}^{4}_{2}He$	$\rightarrow$	${}^{240}_{96}Cm$ (curium)	$+\ 3\,{}^{1}_{0}n$
${}^{244}_{96}Cm$	$+$	${}^{4}_{2}He$	$\rightarrow$	${}^{245}_{97}Bk$ (berkelium)	$+\ {}^{1}_{1}H + 2\,{}^{1}_{0}n$
${}^{238}_{92}U$	$+$	${}^{12}_{6}C$	$\rightarrow$	${}^{245}_{98}Cf$ (californium)	$+\ 5\,{}^{1}_{0}n$
${}^{238}_{92}U$	$+$	${}^{14}_{7}N$	$\rightarrow$	${}^{247}_{99}Es$ (einsteinium)	$+\ 5\,{}^{1}_{0}n$
${}^{238}_{92}U$	$+$	${}^{16}_{8}O$	$\rightarrow$	${}^{250}_{100}Fm$ (fermium)	$+\ 4\,{}^{1}_{0}n$
${}^{253}_{99}Es$	$+$	${}^{4}_{2}He$	$\rightarrow$	${}^{256}_{101}Md$ (mendeleevium)	$+\ {}^{1}_{0}n$
${}^{246}_{96}Cm$	$+$	${}^{13}_{6}C$	$\rightarrow$	${}^{251}_{102}No$ (nobelium)	$+\ 8\,{}^{1}_{0}n$
${}^{252}_{98}Cf$	$+$	${}^{10}_{5}B$	$\rightarrow$	${}^{257}_{103}Lw$ (lawrencium)	$+\ 5\,{}^{1}_{0}n$
${}^{242}_{94}Pu$	$+$	${}^{22}_{10}Ne$	$\rightarrow$	${}^{260}_{104}Ku$ (kurchatovium)	$+\ 4\,{}^{1}_{0}n$

12.12. ISOTOPES, ISOBARS, ISOBARIC ISOTOPES AND ISOTONES

Isotopes of an element are atoms of the same element with different atomic weights. Isotopes possess identical chemical properties because of their identical electronic structure. Isotopes of a particular element have the same number of protons but varying number of neutrons inside their nuclei (page 14). There are other species which possess the same atomic weight but different atomic numbers. Such species are called *isobars*. It follows that isobars have different

chemical properties since they possess different electronic structures. Whereas isotopes occupy the same position in the Periodic Table, isobars are members of different groups of the Table. Chlorine-35 and chlorine-37, oxygen-16 and oxygen-18, hydrogen-1 and hydrogen-2, are common examples of isotopes. Argon-40 and calcium-40, platinum-196 and mercury-196 are examples of isobars. A beta emission does not change the atomic weight but changes the atomic number. Hence the product of beta emission is always an isobar of the mother radioelement. A third case may arise where nuclei with the same atomic weight and the same atomic number may vary only in their radioactive properties. Such species are known as *isobaric isotopes* or as *nuclear isomers*. Zinc-68 on being bombarded by ^1_1H gives off a proton and leads to zinc-69. This freshly synthesized zinc-69 emits gamma radiation till another nuclear isomer zinc-69 is obtained, which decays by beta emission.

Some radioactive elements may have in their nuclei the same numbers of neutrons. Such species are called *isotones*: (88) radium-226 and (89) actinium-227. Isotones display different chemical properties.

In this section an outline of some general methods of separation of isotopes is described. Since isotopes of an element are chemically very similar their separation methods cannot be based on their chemistry. Instead, successful separations can only be achieved when properties, which are mass dependent, are made use of. Some of the important methods are described below:

12.12.1. Diffusion Method: The kinetic energies of two ideal gases A and B at a given temperature being the same we can write:

$$\tfrac{1}{2}m_A v_A^2 = \tfrac{1}{2}m_B v_B^2$$

$$\frac{v_B}{v_A} = \left(\frac{m_A}{m_B}\right)^{\frac{1}{2}} = \text{separation factor } s$$

Graham's law states that at a given temperature the rates of diffusion of two different gases are inversely proportional to the square root of their masses. The above relation holds also for isotopes and their compounds. The lighter isotope (or its compound) will pass through a porous barrier faster than the heavier isotope. The larger the ratio of the molecular weights of the two isotopic species the more efficient is the separation. Hydrogen-deuterium has the most suitable separation factor ($\sqrt{4/2} = \sqrt{2} = 1.414$). This method was originally applied by Aston for the separation of neon isotopes of mass numbers 20 and 22. With the knowledge of nuclear fission reaction of U-235 it became essential to have an enrichment of this fissionable isotope over U-238. For this purpose volatile UF_6 was subjected to gaseous diffusion separation. The separation factor, $\sqrt{352/349} = 1.0043$, is poor. In practice s is around 1.0014. About 10 fold enrichment of U-235 can be achieved in about 2000 stages.

12.12.2. Thermal Diffusion Method: When a gaseous isotopic mixture is introduced into a vertical tube the inside of which is maintained at two different temperatures, the heavier isotope will concentrate in the colder region and the

lighter isotope in the hotter region. A convection current would be set up. Due to thermal diffusion the lighter isotope will move upwards along the hot surface and the heavier isotope will move downwards along the cold surface. In effect, there will be a concentration of the heavier isotope at the bottom and the lighter isotope at the top of the tube. In typical experiments on the separation of isotopes of nitrogen, oxygen and krypton a vertical tube ~3 metres in length and ~1 cm in diameter was used. A platinum wire stretched axially inside the tube was maintained at 500°C, while the outside of the tube was watercooled.

12.12.3. Evaporation and Distillation Methods:

This technique depends on the fact that the rates of evaporation of molecules from a given surface is inversely proportional to the square roots of their masses. If the evaporated molecules are quickly condensed and prevented from returning back to the surface of the remaining liquid, the condensate will be enriched in the lighter isotope. Mercury was allowed to evaporate at 40 ~60°C in an evacuated space and the mercury vapour was condensed on a surface cooled in liquid air, placed at ~2 cm above the evaporating mercury surface (Fig. 12.8). The distance between the evaporating mercury surface and the cold surface is important, and should be smaller than the mean free path of mercury atoms under the prevailing pressure. Under this condition there is an absence of collisions among mercury atoms, and all the evaporating atoms can condense on the cold surface. After some time the bulk of the mercury was removed, the

FIG. 12.8
Separation of mercury isotopes

condensed mercury was allowed to melt, evaporated again and so on. Several repititions gave fractions having densities of 0.99974 and 1.00023 referred to that of the original mercury as 1.

12.12.4. Electromagnetic (Mass Spectrographic) Method:

The essential principle of this method has already been described (page 62). A gaseous isotopic mixture is forced through an electron beam whereby the isotopic mixture gives positive ions of the isotopes. A narrow beam of the positive ions is selected and is accelerated by passage through an electric field. The positive ions with different charge-to-mass ratios spread out. These are then passed through a magnetic field (maintained perpendicular to the electric field) so that the different isotopes follow semicircular path with different radii of curvatures. Under these conditions we have:

$$\frac{e}{m} = \frac{2X}{H^2 r^2}$$

where e and m denote the charge and mass of one of the isotopic species, X the electric field potential, H the magnetic field strength and r, the radius of curvature. For a given charge e, given H and X, the mass m is proportional to the square of the radius of curvature. By placing collecting plates at proper positions the isotopes' can be collected. The method has been applied to the separation of isotopes of lithium, uranium, etc. The method is more suitable for research purpose than for large-scale separation.

12.12.5. Electrolytic Method : Washburn and Urey noted that water obtained from industrial electrolytic cells, which were in operation for a few years for production of oxygen and hydrogen, had a higher density than ordinary water. Therefore on electrolysis of water the lighter isotope of hydrogen $_1^1H$ is evolved initially and the heavier isotope $_1^2H$ continues to accumulate in the remaining water. Alkaline (0.5 N NaOH) water is electrolysed for prolonged period with nickel electrodes and using a large current density till the volume is reduced to about a tenth of the starting volume. At this stage the solution is too much concentrated in NaOH. Electrolysis is suspended, NaOH neutralised with CO_2 gas and the enriched water recovered by distillation. Again the water is made alkaline and electrolysis continued. Starting with a volume of 2311 litres of water 99.0% $_1^2H_2O$ is obtained when the electrolysis reduces the volume to only 82 ml. The nearly pure heavy water on electrolysis liberates heavy hydrogen at the cathode.

This method leads to some concentration of oxygen-18 in the heavy water.

12.12.6. Szilard-Chalmers Separation : During irradiation of a target material by different projectiles different elements are usually produced. In such cases separation of the target element and the product element is not too difficult, since different chemical reactions for the two species are available. However in the case of slow neutron reactions of the (n,γ) type the product nucleus and the target nucleus possess the same atomic number and hence the same chemical reactions. No chemical separation is possible in such cases.

Interestingly during the ejection of a γ-ray photon the product nucleus recoils, and the recoil energy in some cases may be enough to result in the fission of the bond which links the affected atom to the remaining part of the molecule. This effect is known as *Szilard-Chalmers effect*. Due to this effect the product atom will be in a different chemical form from that of the original compound, a separation being possible. Thus when ethyl iodide is irradiated with slow neutrons we have :

$$C_2H_5\ ^{127}I + {}_0^1n \rightarrow C_2H_5\ ^{128}I \rightarrow -- - {}^{128}I + \gamma$$
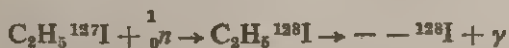
The ethyl iodide, after irradiation, was shaken with a dilute aqueous solution of ordinary iodine. Much of the radioactive ^{128}I was found in aqueous layer. When aqueous $Na^{37}ClO_3$ was subjected to slow neutrons the reaction ^{37}Cl $(n,\ \gamma)$ ^{38}Cl took place. A good amount of the ^{38}Cl was found to pass into aqueous solution as chloride ion which could be precipitated with silver nitrate in the presence of ordinary chloride added as a carrier.

12.13. USES OF ISOTOPES

Isotopes have been of varied utility. Researches in medicine, biology, agriculture, trace analysis and many other fields have been aided tremendously by the use of isotopes. The uses of isotopes may be broadly classified under the heads: (a) medicinal uses (b) uses in analytical chemistry (c) mechanistic studies (d) age determination of old relics, minerals and rocks and (e) agricultural uses.

(a) Radioactive iodine-131 is used in the diagnosis and treatment of thyroid gland disorders. After drinking a solution of sodium iodide containing iodine —131, the radioactive iodine moves preferentially to the thyroid gland. The radiation (beta emission) destroys the malignant cells without affecting the rest of the body.

(b) Usual chemical analyses allow estimation, at best to the tune of milligrams ($\sim 10^{-3}$ gm). Because of the development of sensitive techniques of measurement of radiations it is now possible to detect radiations originating from submicrogram ($\sim 10^{-6}$ gm) quantities. For example, we know that silver ion is quantitatively precipitated from aqueous solution by halide ions. The reaction is quantitative insofar as our ordinary techniques go. A trace amount of silver is still retained in solution, which can be detected by addition of sodium iodide containing iodine—131 and collecting the colloidal silver iodide with another precipitate, say $Fe(OH)_3$. By measuring the radioactivity of the precipitate it is possible to determine the microgram quantities of silver left in the solution.

Cobalt (II) is precipitated from solution by means of β-nitroso-α-naphthol or α-nitroso-β-naphthol. In order to test the efficacy of these two precipitants the cobalt (II) solution was labeled with cobalt-60, a beta emitter. It was observed from beta activity measurements in the filtrate that 0.17 mg cobalt per litre is left in solution when β-nitroso-α-naphthol is the precipitant while 1.5 mg/litre is retained in the second case. We thus conclude that β-nitroso-α-naphthol is a better precipitant for cobalt (II).

Activation Analysis: This method is applicable to those elements which produce artificial radioactivity on bombarding with neutrons or some other nuclear particle. A known amount of a sample containing the element is first irradiated and the radioactivity produced is measured. Then the sample to be analysed is similarly irradiated and the radioactivity produced is compared with the radioactivity shown in the control experiment. The ratio of the two radiation intensities gives the ratio of the amounts of the two elements present in the control experiment and the unknown sample. Neutrons produced in a cyclotron or a laboratory neutron source (eg: $^{210}Po+Be$) may be used. This method has been successfully used in determining trace amounts of arsenic (0.1—1.0 p.p.m.) in germanium, determination of rubidium and caesium in rocks, meteorites, etc.

Isotope Dilution Analysis: The activity per mg. per minute of a radioactive isotope of the element to be analysed is first determined. A known amount of the active isotope is then mixed with a known amount of the sample which is to be analysed. After isotopic exchange has taken place, a small sample is isolated and the radiation of this sample is measured. The decrease in the radiation activity

gives a measure of the inactive isotope present in the sample under analysis. This technique of analysis finds extensive use in biological researches.

(c) Isotopes have played a key role in the evaluation of reaction mechanisms, particularly in organic chemistry. One reaction which has been studied in this manner is the process of photosynthesis, for which the following overall reaction can be written:

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

The reaction takes place in several complicated steps. Whether the oxygen gas originates from the oxygen of CO_2 or from the oxygen of H_2O, has been settled by the use of oxygen-18. It was definitely established by mass spectrometric analysis of the oxygen (oxygen-18 is not radioactive) that any oxygen-18 introduced into water showed up as O_2 gas. Carbon dioxide with oxygen-18 could not influence the evolved oxygen. Therefore it is evident that the elementary oxygen given out by green plants is formed from water, and not from carbon dioxide. Calvin and his group did extensive studies on the mechanism of photosynthesis. 1961 Nobel Prize in chemistry went to Calvin as a mark of recognition of his brilliant researches.

When H_2O_2 reacts with strong oxidants such as PbO_2, MnO_4^-, $Cr_2O_7^{2-}$, etc oxygen gas is produced:

$$PbO_2 + H_2O_2 \rightarrow PbO + H_2O + O_2$$

It was a long standing controversy whether the O_2 comes entirely from H_2O_2 or partly from the oxidant:

$$Pb\,O \quad \overline{O + O} \quad O\,H_2 \rightarrow PbO + H_2O + O_2$$

$$Pb\,O \quad \overline{O} + O{-}O \qquad \rightarrow PbO + H_2O + O_2$$
$$\qquad\qquad \underset{H\ \ H}{\big|\ \ \big|}$$
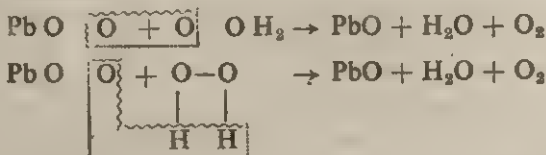
Oxygen-18 labeled H_2O_2 was used and mass spectrometric analysis of the oxygen produced in the reaction proved definitely that all the O_2 came from H_2O_2. Thus the $O{-}O$ link of H_2O_2 is not destroyed during the reaction.

In the esterification process two mechanisms are possible: (i) the OH of the carboxylic acid may react with the hydrogen of the alcohol to eliminate H_2O and (ii) the OH of the alcohol may react with the carboxyl hydrogen of the acid. If the alcohol oxygen is labeled with O-18, then according to case (i) the ester will carry the O-18. But in the other case (ii) the ester will have no O-18; instead the released H_2O will carry the O-18. In reality both possible mechanisms have been observed for different combinations of alcohols and acids.

(i) $\quad R{-}C{\overset{\displaystyle O}{\underset{\displaystyle OH}{\big\langle}}} \quad + HO^*{-}R' \rightarrow R{-}C{\overset{\displaystyle O}{\underset{\displaystyle O^*{-}R'}{\big\langle}}} \quad + H_2O$

(ii) $\quad R{-}C{\overset{\displaystyle O}{\underset{\displaystyle OH}{\big\langle}}} \quad + HO^*{-}R' \rightarrow R{-}C{\overset{\displaystyle O}{\underset{\displaystyle O{-}R'}{\big\langle}}} \quad + H_2O^*$

(O* stands for the labeled O—18)
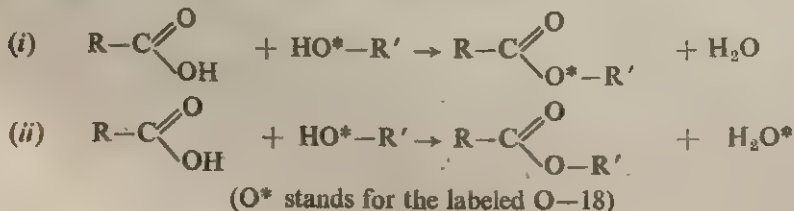
(d) Libby has developed a method of determining the age of organic material based on the accurate determination of the ratio of carbon-14 to carbon-12. Carbon-14 is produced in the atmosphere by the interactions of neutrons (from cosmic radiation) with ordinary nitrogen;

$$^{14}_{7}N + \, ^{1}_{0}n \rightarrow \, ^{14}_{6}C + \, ^{1}_{1}H$$
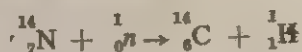
The carbon-14 ultimately goes over to carbon-14 dioxide. A steady state concentration of one ^{14}C to 10^{12} ^{12}C is reached in the atmospheric CO_2. This carbon dioxide is taken in or given out by plants and plant-eating animals or human beings so that they all bea this ratio. When a plant or animal dies the steady state is disturbed since there is no fresh intake of atmospheric CO_2 and the dead matter is out of equilibrium with the atmosphere. The ^{14}C continues to decay so that after a number of years only a fraction of it is left in the dead matter. Therefore the ratio of the $^{14}C/^{12}C$ drops from the steady state ratio in the living matter.

$$^{14}_{6}C \rightarrow \, ^{14}_{7}N + \, ^{0}_{-1}e(t_{\frac{1}{2}} = 5760 \text{ years}),$$

By measuring this ratio and comparing it with the ratio in living plants one can estimate when the plant died.

Problem: A piece of wood was found to have $^{14}C/^{12}C$ ratio 0.7 times that in a living plant. We wish to calculate the approximate period when the plant died.

$$k = \frac{0.693}{5760 \text{ years}} = 1.20 \times 10^{-4} yr^{-1}$$

$$\log \frac{N_0}{N} = \frac{kt}{2.303}$$

$$\therefore \log \frac{1.000}{0.700} = \frac{1.20 \times 10^{-4} yr^{-1} \times t}{2.303}$$

$$\therefore \quad 0.155 = \frac{1.20 \times 10^{-4} yr^{-1} \times t}{2.303}$$

$$\therefore \quad t = \frac{2.303 \times 0.155}{1.20 \times 10^{-4} \times yr^{-1}} = 2970 \text{ years.}$$

A knowledge of the rate of decay of certain radioactive isotopes helps to determine the age of various rock deposits. Let us consider a uranium containing rock formed many many years ago. The uranium started to decay giving rise to the uranium-238—lead-206 series. The half lives of the intermediate members being small compared to that of uranium-238 (4.5×10^9 years), it is reasonable to assume that those uranium atoms that started decaying many many years ago must have been completely converted to the stable lead-206 during this extra long period. The uranium-238 remaining and the lead-206 formed must together account for the uranium-238 present at 'zero' time, that is, when the rock solidified.

Thus both N_0 and N are known and k is known from a knowledge of the half life of uranium-238. Therefore the age of the rock can be calculated.

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Problem: A sample of uranium ($t_{\frac{1}{2}} = 4.5 \times 10^9$ yr) ore is found to contain 11.9 gm of uranium-238 and 10.3 gm of lead-206. From these data we calculate the age of the ore thus:

$$k = \frac{0.693}{4.5 \times 10^9 \text{ yr}} = 0.154 \times 10^{-9} \text{ yr}^{-1}$$

11.9 gm of uranium-238 = 0.05 moles of uranium-238
10.3 gm of lead-206 = 0.05 „ „ lead-206

Moles of uranium-238 present in the ore at zero time = 0.05 + 0.05 = 0.10 mole

Then $\dfrac{N_0}{N} = \dfrac{0.10 \text{ mole}}{0.05 \text{ mole}} = 2$

$2.303 \log \dfrac{N_0}{N} = kt$ ∴ $t = \dfrac{2.303}{0.154} \dfrac{\log 2}{10^{-9} \text{ yr}^{-1}} = 4.5 \times 10^9$ yr.

The age of the ore is thus 4.5×10^9 yr. The data of 0.05 moles of uranium and 0.05 moles of lead in the ore immediately indicates that one half life had elapsed since the formation of the ore.

Age of the ore can also be obtained from a knowledge of the amount of helium gas trapped in the ore during decay processes. This helium is formed from alpha particles during radioactive disintegration. One gram of uranium in a state of equilibrium with its decay products produces ~10^{-7} ml of helium per year. If we know by analyses the amount of the uranium and helium in the ore the age of the ore can be calculated.

$$\text{Age} = \frac{\text{ml. of helium per gm of the ore} \times 10^7}{\text{amount of uranium per gm of the ore}}$$

This relation assumes that no helium has been lost to the atmosphere, which is most unlikely. Therefore the age determined from helium analysis is likely to be lower than the real age of the ore.

The calculation becomes more complicated when the rock also contains Th-232 which is the starting member of the 4n disintegration series (page 302). In the event of both U-238 and Th-232 being present in the ore we have helium from two sources. The amount of helium released by Th-232, while in equilibrium with its disintegration products, is about that released by one-third its weight of U-238. The above relation then takes the form:

$$\text{Age (in years)} = \frac{\text{ml. of helium per gm. of the ore} \times 10^7}{(\text{amount of uranium} + 0.3 \times \text{amount of thorium})}$$
per gm. of the ore.

Problem: One Kg. of an ocean sediment contains 1.50 mg of uranium-238, 4.20 mg of thorium-232 and 6.0×10^{-3} ml. of helium. What is the age of the sediment ?

Amount of U-238 per gm of the sediment = $1.5 \times 10^{-3} \times 10^{-3}$ gm.
Amount of Th-232 per gm of the sediment = $4.2 \times 10^{-3} \times 10^{-3}$ gm.

$$\text{Age of the sediment} = \frac{6.0 \times 10^{-3} \times 10^{-3} \times 10^7}{(1.5 + 0.3 \times 4.2) \times 10^{-3} \times 10^{-3}} \simeq 2 \times 10^7 \text{ years.}$$

(e) Plants assimilate important constituents from any fertiliser added to the soil as also the same constituents from the soil itself. A problem relates to the determination of the relative proportion of intake of essential matter from the two sources. For instance, plants are given some superphosphate of lime, $Ca(H_2PO_4)_2$ labeled with radioactive phosphorus-32, a beta emitter. (Some radioactive phosphoric acid $H_3{}^{32}PO_4$ is first produced from radioactive phosphorus. This radioactive phosphoric acid is then mixed with ordinary phosphoric acid and the mixture converted to the superphosphate). Specific activity of this fertiliser is determined. Plants are given this fertiliser and after a period of growth the plants are burnt. The quantity of phosphorus present in the ash is determined by chemical analyses. Assuming that the plant does not distinguish between radioactive superphosphate and non-radioactive superphosphate, a measurement of specific activity of the ash will tell us the amount of the labeled fertiliser consumed by the plant. The remaining phosphate in the ash must have been consumed by the plants from the soil itself.

12.14. NUCLEAR BINDING ENERGY AND PACKING FRACTION

12.14.1. Nuclear Binding Energy: We can calculate the expected mass of any nucleus from a knowledge of the nuclear composition and the masses of proton and neutron. Such calculation shows that the calculated mass of a nucleus is always greater than the experimentally determined mass. This difference is variously called as *mass defect, mass deficit* or *mass decrement*. For example, the helium nucleus $_2^4He$ has the following data:

mass of 2 protons $= 2\,(1.00728)\ amu = 2.01456\ amu$
mass of 2 neutrons $= 2\,(1.00867)\ amu = 2.01734\ amu$
$\overline{4.03190\ amu}$

actual mass of $_2^4He$ $= 4.0015\ amu$

Hence $(4.03190 - 4.00150) = 0.03040\ amu$ is the mass defect. The mass defect has been transformed into the binding energy of the nucleus by Einstein equation $E = mc^2$. The binding energy of a nucleus may be considered to be the energy released in the formation of the nucleus from neutrons and protons. Therefore in order to split up the nucleus into neutrons and protons, of which it is formed, an energy equal to the nuclear binding energy must be supplied.

Substituting the value of c as 3.00×10^{10} cm/sec in Einstein equation we have:

$$\text{Energy (in ergs)} = 9.00 \times 10^{20} \times \text{mass}$$

so that 1 gm $= 9.00 \times 10^{20}$ ergs. Again 1 erg $= 6.24 \times 10^5$ Mev (Mev = million electron volts) and since 1 gm $= 6.02 \times 10^{23}$ amu therefore 1 amu $= 931$ Mev. The binding energy of $_2^4He$ nucleus thus becomes:

Binding energy in Mev $= 0.03040\ amu \times 931\ Mev/amu = 28.3\ Mev,$

Since the helium nucleus contains a total of four nuclear particles (nucleon), we have:

$$\text{Binding energy per nucleon} = \frac{\text{Total binding energy of the nucleus}}{\text{number of nucleons}}$$

$$= \frac{28.3 \; Mev}{4} = 7.07 \; Mev$$

Binding energies vary greatly with the composition of the nucleus. An idea of the relative stability of the stable nuclei of the different elements can be had from a plot of the binding energy per nucleon of the nucleus against the mass number of nucleus (Fig. 12.9). A study of the figure reveals three interesting points. The first point is that the curve shows a maximum around the nuclei of mass
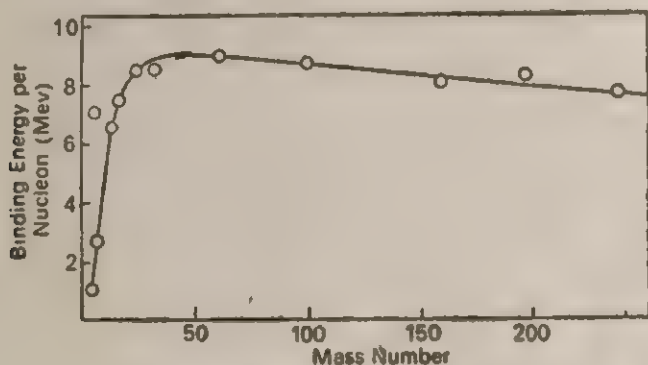
FIG. 12.9. Binding energy of nuclei

number ~60. Secondly nuclei of very heavy elements like uranium have comparatively low binding energy and will be apt to splitting into smaller nuclei. Such splitting (nuclear fission) will release great amounts of energy. Thirdly the binding energy per nucleon rises sharply from the isotopes of hydrogen to those of the next heavier elements like helium or lithium. Thus fusing together (nuclear fusion) of hydrogen atoms so as to lead to helium nuclei will provide vast amounts of energy. In fact, the energy available from nuclear fusion is far greater than the energy obtained from the fission of an equal mass of a very heavy element.

Factors determmining nuclear stability : It is observed that after an abrupt rise in the binding energy per nucleon (E_b/A; E_b = total binding energy and A = total nucleons) among the lightest nuclei, the binding energy per nucelon changes only slightly and attains a value of 8 Mev per nucleon. Because of the maximum in E_b/A for nuclei of mass around 60, the fission of a heavy nucleus to a pair of nuclei of mass around 60 will release lot of energy. Again the fusion of two of the lightest nuclei will also lead to release of vast energy.

Since for elements of mass number greater than 20 there is only slight changes in the binding energy per nucleon we may roughly write :

$E_b/A \simeq$ a constant i.e $E_b \simeq$ a constant $\times A$. Thus the total binding energy of a nucleus is roughly proportional to A i.e the number of nucleons. This indicates

that nuclear binding forces are short range forces i.e one nucleon exerts attractive forces only on its closest neighbours. If the attractive force would have been of the long range type then each of the A nucleons would have been attracted to $(A-1)$ nucleons so that E_b would be proportional to $A(A-1)$ instead of to A only.

The nuclear attractive force is independent of charge. However because of a Coulomb repulsion among protons, the net binding energy of two protons is less than that of two neutrons. If a correction is made for the coulomb repulsion between two protons the attractive nuclear binding energy is around 14.1 Mev per nucleon. In view of the existing Coulomb repulsion beween protons the net value of ~8 Mev is observed.

It is assumed that the nucleons are present as close-packed spheres, each with 12 nearest neighbours. Since it requires two nucleons to form a bond there will be 6 bonds per nucleon. Then the attractive energy between a single pair of nucleons is 14.1/6 i.e 2.3 Mev.

A semiempirical expression for the total nuclear binding energy has been derived, which runs as:

$$E_b = 14.1A + 13A^{2/3} - \frac{0.6Z^2}{A^{1/3}}$$

The term $14.1A$ represents the total attractive binding energy. However the surface nucleons do not have 12 nearest neighbours and so cannot contribute to the extent of 14.1 Mev. The number of the surface nuclei varies as the surface area which again varies as the square of the nuclear radius i.e $A^{2/3}$. The Coulomb repulsion between protons is indicated by the third term on the right hand side. Coulomb repulsion is directly proportional to Z^2 (Z = nuclear chage = number of protons) but inversely proportional to the nuclear radius i.e to $A^{1/3}$. The negative signs in the above expression indicate loss of energy from $14.1A$. Experimental studies have shown that the radius of a nucleus of A nucleons varies as $A^{1/3}$.

12.14.2. Packing Fraction: Aston had introduced a term, *packing fraction*, which also indicated the extent of nuclear stability:

$$\text{Packing Fraction} = \frac{\text{Actual mass of an isotope} - \text{mass number on physical scale}}{\text{mass number}} \times 10,000.$$

Mass number of an element indicates the total number of nucleons inside the
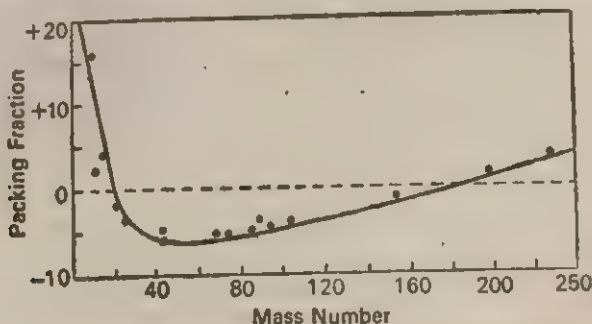
FIG. 12.10. Packing fraction curve for stable nucleides

nucleus. Isotopic mass on the physical scale could be smaller or larger than the mass number of the isotope. Thus both positive and negative values are possible. On the contrary nuclear binding energy has as its numerator the energy equivalent of the difference between the calculated nuclear mass and actual mass. The calculated nuclear mass being always greater than the actual mass, binding energy is always positive. Most negative packing fraction values are shown by elements of mass number 50—60. A negative value indicates that the isotopic mass is less than the mass number of the isotope. This means that some mass has been lost to make the particular isotope. It follows that such isotopes must have high stability i.e. high nuclear binding energy (cf. Fig. 12.9 and 12.10). Where the packing fraction curve sharply falls the binding energy curve sharply rises. Increasingly positive packing fractions for high mass numbers parallel the slowly decreasing binding energies. However, packing fractions have lesser significance than nuclear binding energies.

12.14.3. Mass Number and Atomic Weight: At this stage we are in a position to answer the oft-asked question why mass number is a whole number while atomic weight is fractional. Mass number is the total number of nucleons (i.e. protons and neutrons) present in the nucleus and obviously is a whole number. On the other hand atomic weight is the averaged weight of the nucleons of the different isotopic species based on their relative abundance in nature. Moreover during the formation of the nucleus some mass corresponding to mass defect is lost. Both these factors contribute to the fractional atomic weight of an element. Also note that the proton mass (1.00728 *amu*) and neutron mass (1.00867 *amu*) are also not whole numbers.

12.15. NUCLEAR BINDING FORCES

The nature of the forces that hold together neutrons and protons inside the nucleus is an intriguing one. It is said that physicists have expended maximum man hours of mental labour and experimentation after this problem than have been given to any other scientific question in the history of mankind. Our usual laws would predict that the nucleus would not hold together at all, instead all the nucleons should flee from one another. A scrutiny of the binding energies of some simple nuclei point, on the other hand, to the existence of proton-neutron $(p-n)$, proton-proton $(p-p)$ and neutron-neutron $(n-n)$ forces of attraction of formidable magnitude.

The nuclear binding forces are short-range forces operating over very short distance $\sim 10^{-13}$ cm. If the binding forces were of the electrostatic type then the nuclear binding energy would increase roughly as the square of the number of particles inside the nucleus. In reality the nuclear binding energy is proportional to the number of nucleons. As the number of nucleons increase, the nucleons get further apart and so far as these very short range forces are concerned, the nucleons go out of range of all but a few other nucleons only. Against this force there is the electrostatic energy of repulsion between the protons, varying as the

square of the nuclear charge, so that this repulsive contribution of the binding energy per nucleon is proportional to the nuclear charge. These factors influencing nuclear stability are illustrated in Fig. 12.11.

These short range forces are, in a crude way, analogous to the chemical forces operating in covalent molecules. In such compounds there are strong covalent bonds between the atoms forming the molecule but only very weak forces in between molecules. Chemical bonding force is a type of saturation force. The nuclear binding forces do not extend beyond the bounds of the nucleus, and hence these forces are also of the saturation type. In covalent molecules atoms are held together by the sharing of electrons, the sharing being the sum total expression of structures among which exchange takes place. In such cases the actual structure can be regarded as a combination of all the possible individual structures and the energy of the actual structure is lower than the energy of any of the individual

FIG. 12.11. Diagram showing the relative influence of different factors in nuclear stability.

structures. These ideas can be extended to nuclear particles as well. It is but natural to conjecture that an electron (positive or negative) may be the particle responsible for the exchange forces but calculation shows that it can serve such a role only over a range of 10^{-11} cm, a range much larger than the average nuclear radius of 10^{-13} cm. Yukawa then postulated the existence of a new charged particle which had the same charge as that of the electron but much larger mass (200—300 times that of the electron). This was named pi-meson (*pion*) which could have a positive charge (π^+, positive *pion*) or a negative charge (π^-, negative *pion*). Yukawa postulated that when a proton and a neutron interact, the proton may emit a positive meson which is absorbed by the neutron. In this process the proton loses its positive charge and becomes a neutron, while the neutron gains the positive charge and turns into a proton. The same overall result is obtained when the neutron emits a negative meson which is absorbed by the proton.

$$\text{proton} \ (\cdot \uparrow \text{spin}) \rightleftharpoons \text{neutron} \ (\downarrow \text{spin}) + \pi^+$$
$$\text{neutron} \ (\downarrow \text{spin}) \rightleftharpoons \text{proton} \ (\uparrow \text{spin}) + \pi^-$$
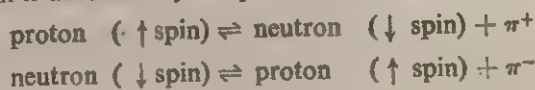
This mutual exchange leads to the pairing of the spins of the nucleons. The next problem was to offer explanations for the binding of like particles, namely the $p-p$ and the $n-n$ forces. A proton cannot absorb a positive meson, since it is already positively charged. Therefore no single charged meson could transmit a force between protons. A neutral meson was therefore conceived which might be responsible for the exchange forces between proton and proton, and between

neutron and neutron. The exchange forces will eventually lead to the spin pairing of the nucleons. Charged mesons and neutral mesons have all been detected. They are very unstable outside the nucleus.

At a distance of 10^{-13} cm (radius of the atom $\sim 10^{-8}$ cm) the nuclear force of attraction between two protons is about forty times as strong as the repulsive force between them. At four times that distance the nuclear attractive force has dropped off to the same strength as the electric repulsive force and at twenty times that distance the repulsive force is million times stronger. Therefore as the size of the nucleus continues to increase there occurs a decrease in the nuclear attractive forces and an increase in the repulsive forces. Heavy nuclei thus become unstable and show spontaneous disintegration.

Nuclear Shell Model: Magic Numbers: In the Chapter on magnetochemistry we have observed that a moving electron has l and s quantum numbers—which may under the strong influence of the nucleas may combine to produce resultant quantum number j. Like the extranuclear electrons the nucleons i.e. the protons and the neutrons also obey Pauli exclusion principle. Each nucleon has a spin quantum number $\frac{1}{2}$ i.e. $m_s = \pm \frac{1}{2} \left(\frac{h}{2\pi} \right)$. Just as for each electronic orbital there can be at most a paired spin of electrons so also is the case for any nuclear level. Each nucleon also possesses an orbital angular quantum number l which may have values 0, 1, 2, 3, 4, etc. The spin-orbit coupling of the nucleons will give rise to j states which will have values $l + \frac{1}{2}$ or $l - \frac{1}{2}$. Each j level has a multiplicity of $2j + 1$ i.e. each level can have a maximum of $2j + 1$ protons and $2j + 1$ neutrons. The nuclear shells have their own principal quantum number, n, with sublevels $l = s, p, d, f$, etc. However unlike electronic levels their orders are $1s, 1p, 1d, 2s, 1f$, etc. Depending on the values of $j = \frac{1}{2}(= 0 + \frac{1}{2}); j = 1 + \frac{1}{2} = \frac{3}{2}$ or $1 - \frac{1}{2} = \frac{1}{2}; j = 2 + \frac{1}{2} = 5/2$ or $2 - \frac{1}{2} = \frac{3}{2}$ etc. the number of nucleons of each kind i.e. either proton or neutron will be $2j + 1$ i.e. 2 (for $l = 0$), $4 + 2 = 6$ (for $l = 1$), $6 + 4 = 10$ (for $l = 2$), 2 (for $2s = 0$) etc. Thus successive shells will be filled with either protons or neutrons when $2, 2 + 6 = 8, 2 + 6 + 10 + 2 = 20$. 28, 50, 82 and 126 particles of that particular kind (protons or neutrons) in the lowest energy levels. These numbers are known as *magic numbers.* A nucleus with magic numbers of either protons or neutrons is quite stable. Furthermore a particular nucleus containing magic numbers of both neutrons and protons attains an exceptional stability. Thus $_2^4He_2$; $_8^{16}O_8$; $_{20}^{40}Ca_{20}$ and $_{82}^{208}Pb_{126}$ nuclei are extremely stable. It is of interest to note that because of the extreme stability associated with such lead nuclei, the three naturally occurring radioactive series end in lead—206, lead—207 and lead—208.

12.16. NUCLEAR FISSION, NUCLEAR SPALLATION AND NUCLEAR FUSION

12.16.1. Nuclear Fission: A study of the artificial transmutation reactions so far described reveals that such nuclear reactions are good enough to change

the target nuclei by no more than a few atomic numbers. In the late thirties how-
ever physicists encountered a nuclear reaction initiated by neutrons on uranium-
235 isotope, which called for revolutionary explanations. Analysis of the reaction
products pointed to the presence of two elements of atomic numbers, which were
widely different from that of uranium. The reaction was complicated further by
the simultaneous occurrence of more than one nuclear reactions:

$$
{}^{235}_{92}U + {}^{1}_{0}n
\begin{cases}
\rightarrow {}^{90}_{37}Rb + {}^{144}_{55}Cs + 2\,{}^{1}_{0}n \\[2ex]
\rightarrow {}^{87}_{35}Br + {}^{146}_{57}La + 3\,{}^{1}_{0}n \\[2ex]
\rightarrow {}^{96}_{36}Kr + {}^{137}_{56}Ba + 3\,{}^{1}_{0}n
\end{cases}
$$
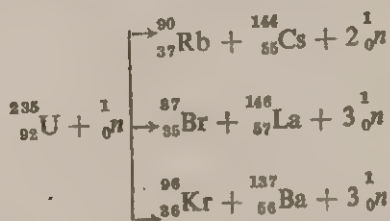
Thus the uranium-235 nucleus suffers splitting or fission into smaller fragments.
The products of fission belong to two groups—one having mass numbers 85 to
104 while the other has mass numbers 130 to 149. However mass number ~ 95
and ~ 139 seem to dominate the fission products.

Although uranium-238 shows spontaneous disintegration its 235 isotope does
not undergo spontaneous fission. The necessary activation energy for the fission
is lacking. The situation can be explained on the *liquid drop model*. A liquid drop
retains its spherical shape due to surface tension. On the application of sufficient
energy to counter the surface tension the liquid drop may be forced to move from
a sphere to an ellipsoid, then to a dumbbell and finally into two spheres. Similarly
if sufficient energy is introduced into a uranium nucleus via addition of a neutron,
then the compound nucleus might behave as a liquid drop under the influence
of a distorting force. Such an activated uranium nucleus may ultimately break
up into two nuclei of close mass numbers.

Uranium-235 is split by *slow (thermal)* neutrons of energy 0.03 *ev* as also by
fast neutrons of energy ~ 1 *Mev*. Thermal neutrons are those neutrons whose
average kinetic energy has been reduced to thermal energy (kT) which is a small
fraction of an electron volt at ordinary temperature. Fast neutrons are reduced
to thermal neutrons by passage through a good moderator. A good moderator
does not absorb neutrons to any appreciable extent but significantly reduces the
speed of the neutrons in a few collisions. Heavy water and graphite are used as
moderators in nuclear reactors.

Uranium-238 suffers fission by fast neutrons only. Plutonium-239 undergoes
nuclear fission by thermal neutrons. Uranium-238 goes to plutonium-239 by the
following scheme:

$$
{}^{238}_{92}U + {}^{1}_{0}n \text{ (fast)} \rightarrow {}^{239}_{92}U + \gamma \rightarrow {}^{239}_{93}Np + {}^{0}_{-1}e
$$

$$
\downarrow
$$

$$
{}^{239}_{94}Pu + {}^{0}_{-1}e
$$
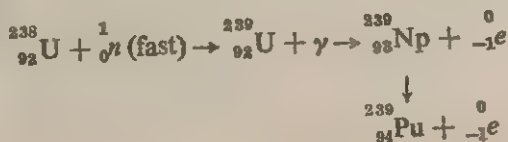
Thorium-232 is changed to uranium-233 via neutron capture and subsequent beta emission. Uranium-233 is fissionable:

$$_{90}^{232}\text{Th} + _{0}^{1}n \rightarrow _{90}^{233}\text{Th} \rightarrow _{91}^{233}\text{Pu} + _{-1}^{0}e \rightarrow _{92}^{233}\text{U} + _{-1}^{0}e$$
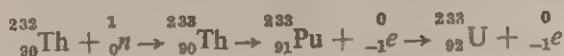
Fission reactions are accompanied by evolution of large amounts of energy due to the conversion of mass decrement into energy. Take the following example:

$$_{92}^{235}\text{U} + _{0}^{1}n \rightarrow _{35}^{87}\text{Br} + _{57}^{246}\text{La} + 3 _{0}^{1}n$$
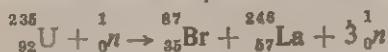
Considering the nuclear masses we have:

U-235	= 234.99340 amu	Br-87	= 86.902800 amu
neutron	= 1.00867 amu	La-146	= 145.886500 amu
		3 neutrons	= 3.02601 amu

= 236.00207 amu	= 235.8151310 amu

Mass defect   = 0.186760 amu

energy released   = 0.186760 amu × 931 Mev/amu

                 = 173.873 Mev

(lg. $= 6.02 \times 10^{23}$ amu; 1 amu $= 931$ Mev; 1 gm $= 2.15 \times 10^{10}$ KCal). It is to be noted that the mass defect for the fission of one atom of U-235 is numerically equal to the change in mass in gm for the fission of 1 gm-atom i.e. for 235 gm of U-235. So the energy released from the fission of one gram of U-235 is given by 0.18676 g/235 $\simeq$ 0.0008 g which is $\simeq$ 17,000,000 K Cal of energy. Compare alongside that heat of combustion of coal (8 K Cal/gm) and T.N.T. (0.66 K Cal/g). Thus fission of 1 gm of U-235 releases as much energy as is obtained from the combustion of 2083 Kg of coal.

It is quite likely that during fission some neutrons will be lost. If loss of neutrons can be minimised then these neutrons can sustain further nuclear disintegration and ultimately a chain reaction will develop. To minimise neutron loss the area/volume ratio of the target should be small. For a given volume, a sphere has the smallest area (area $= 4\pi r^2$; volume $= 4\pi r^3/3$; area/volume $= 3/r$). Further, the area/volume decreases with increasing radius i.e. with the size of the target. *Critical size of the target is that size for which there is no net gain in the number of neutrons for sustaining the chain reaction i.e. for which neutron loss by escape is the same as the neutron produced in the fission reaction.* When the target exceeds the critical size more neutrons are produced than can escape, and hence a self sustained chain reaction occurs. Critical size of U-325 is around 9 Kg.

Based on the above ideas the first atomic bomb was developed.

The atomic bomb consists of a design to bring together, at the time of the explosion, two chunks of uranium-235 of sub-critical size which together will exceed the critical mass. The stray neutrons in the atomosphere are sufficient to start the chain reaction. The chain reaction releases in less than a millionth of a second huge amounts of energy which spells savage destruction.

Nuclear Cross Section: This may be defined as the effective area of cross section of one nucleus of a particular species for a certain reaction. A high value

of nuclear cross section of a reacting species indicates a high efficiency for the reaction. If the surface of the target species contains N nuclei per sq-cm and if σ represents the area in sq-cm per nucleus which is effective for the reaction, then $N\sigma$ is the effective area per sq. cm of the total surface of the target. If I is the number of the bombarding particles striking a unit area of the target in a given time, then A—the number of the target nuclei reacting effectively in a given time— is given by $A = \sigma NI$. Then A/N is the fraction of the target nuclei undergoing reaction. A/N also represents the number of reacting nuclei for every single target nucleus. Manipulation of the above relation also shows that σ, the nuclear cross section, is equal to A/NI. This means that σ is the fraction of the particles falling on 1 sq. cm. of the target which reacts with a single nucleus. It follows the greater is the efficiency of the transmutation reaction the greater the fraction of the incident particles actually reacting is.

Suppose I_0 number of incident particles fall on a target sheet of 1 sq. cm area and thickness x cm and I represents the number of particles emerging on the other side of the sheet then:

$$\frac{I}{I_0} = e^{-NX\sigma}$$

N represents now the number of target nuclei per c.c. It is thus possible to evaluate σ.

Controlled Nuclear Reactions for Peaceful Purposes: Scientists have succeeded in controlling nuclear chain reactions so that these become useful in generating power for mankind. A great variety of nuclear reactors are now in operation in various parts of the world. Nuclear power generators have the following basic components:

1. *Fuel:* Natural uranium enriched with uranium-235 or plutonium-239 is used in the form of plates often alloyed with aluminium. These uranium plates are separated from each other by neutron-moderating material like graphite.

2. *Control Rods:* Reactors are so designed that rods of cadmium or boron can be inserted. These are good absorbers of neutrons so that the rate of fission reaction can be controlled by pushing in or pulling out of the control rods.

3. *Moderators:* To prevent fission reactions going out of control all reactors are provided with moderators so as to reduce the speed of the neutron. Graphite, water and D_2O are good moderators.

4. *Coolant:* The energy produced in reactors is given off primarily as heat. The coolant—usually D_2O, H_2O or even a molten mixture of sodium and potassium—conducts away the heat to a heat exchanger. In the heat exchanger the heat is utilised to generate steam which in turn is used to drive turbogenerators for producing electricity.

5. *Shielding:* The intense radiation produced in the interior of the reactor is contained by the use of water, concrete or both. Lead shielding is also used.

Nuclear power plants have come to stay in India with the commissioning of the Tarapur unit near Bombay and Ranapratapsagar unit in Rajasthan. Atomic power stations are also being set up at Kalapakkam in Tamil Nadu and Narora

in Uttar Pradesh. Nuclear powered ships of the USA and the USSR ply the high seas. If the nuclear reactions in power plants go beyond control tragedy like that in Chernobyl (USSR) will befall, leading to devastating effect on our environment.

Scientists fear that the natural stock of fissionable U-235 cannot serve mankind for more than a century. Fission of more abudant U-238 isotope via Pu-239 appears to be a more attractive course. A still more attractive possibility is the fission of Th-232 via U-233. Future hope of mankind lies in the ability of the scientists and engineers to produce reactors capable of giving fissionable isotopes from more abundant elements like lead, thorium and mercury.

12.16.2. Nuclear Spallation: When elements of intermediate range of mass number and atomic number are bombarded by high energy alpha particles, protons or deuterons they do not undergo nuclear fission into two fragments of close mass; instead these nuclei are split into a variety of nuclei of lower masses and atomic numbers. Such nuclear reactions are called nuclear spallation. Thus, protons of moderate energy splits silver into cobalt, scandium and neutrons:

$$_{47}^{107}Ag + _{1}^{1}H \longrightarrow _{27}^{61}Co + _{21}^{45}Sc + 2_{0}^{1}n$$
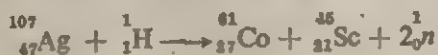
Very high energy protons split $_{50}^{118}Sn$ into $_{31}^{62}Ga$ alongwith the liberation of seven neutrons and ten alpha particles:

$$_{50}^{118}Sn + _{1}^{1}H \longrightarrow _{31}^{72}Ga + 7_{0}^{1}n + 10_{2}^{4}He$$

The identification of so many products being formidable spallation reactions have been studied only in a few cases.

12.16.3. Nuclear Fusion: An inspection of Fig. 12.9 reveals that the binding energy per nucleon of the light element rises very sharply with increasing mass. This means that large amount of energy will be released during their formation via fusion of still lighter nuclei. Take the following nuclear reaction:

$$4_{1}^{1}H \longrightarrow _{2}^{4}He + 2_{+1}^{0}e$$

Mass defect $= (4 \times 1.00728 \ amu)-(4.00150 \ amu + 2 \times .000549 \ amu)$
$= .026522 \ amu$

Remembering that the mass defect in grams for 4 gm atoms of hydrogen is numerically equal to the mass defect in *amu* for 4 atoms of hydrogen we have:

$$\text{energy released} = \frac{.026522g}{4} = .0066305 \times 2.15 \times 10^{10} \ KCal$$

$$= 14.25 \times 10^{7} \ K \ Cal$$

Thus nuclear fusion of light nuclei liberates far greater energy than is released in a nuclear fission.

In nuclear fission a neutral particle ${}_0^1 n$ approaches uranium-235 so that there is no repulsive barrier to the approach of the neutron. But in nuclear fusion positively charged nuclei have to approach each other in order to initiate a fusion reaction. Therefore the approaching nuclei must be supplied with sufficient kinetic energy in order to overcome the repulsive barrier. In the hydrogen bomb, where nuclear fusion of hydrogen nuclei is made use of, the kinetic energy needed to overcome the repulsive barrier is supplied by extremely high temperature attained through the initiation of a nuclear fission reaction as a preliminary step to the fusion reaction.

It is believed that the following net nuclear fusion reaction occurs in the interior of the sun where the temperature is of the order of twenty million degrees:

$$4{}_1^1H \rightarrow {}_2^4He + 2{}_{+1}^{0}e + \text{energy}$$
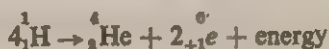
It is also believed to be the case inside the distant stars. It has been calculated that during this energy output the sun is losing its mass at the rate of about four million tons per second. Even at this fantastic rate of loss of mass our Sun-God will continue to bless us on this good earth for thirty billion years. Blessed indeed we are !

STUDY QUESTIONS

1. Discuss which of the following unstable isotopes will decay by electron or positron mission : ${}_5^{12}B$, ${}_6^{11}C$ and ${}_8^{14}O$.

2. Comment on the following statements:

(a) ${}_8^{16}O$ has the same chemical properties as ${}_8^{18}O$

(b) radioactive Na^+ behaves in the same way as radioactive Na atom

3. The half-life of ${}_{81}^{199}Tl$ is 22 minutes. Now calculate

(a) the rate constant for the decay

(b) the fraction of the sample left after one hour

4. The half life of uranium-238 is 4.5×10^9 years. What is the mole ratio of uranium to lead in a rock of age 2×10^9 years.

5. ${}_1^2H$, ${}_5^{10}B$, ${}_6^{12}C$ are stable nucleides. Write nuclear equations for radioactive decay of ${}_1^3H$, ${}_5^8B$, ${}_5^{12}B$, ${}_6^{10}C$.

6. What are the types of radiation emitted by radioactive substances. Describe the characteristics of these radiations. How these rays have been identified?

7. Present an account of the contributions of radioactivity towards elucidation of atomic structure.

8. A painting, being claimed to be an original or Raphael (1483—1520), is analysed by carbon -14 technique. A small piece of the canvas gives the carbon-14 content to be 0.95 of that in living plants. Is the painting a forgery?

9. Write balanced nuclear reaction:

(a) for the loss of an alpha particle by $_{90}^{238}Th$

(b) for the loss of a beta particle by $_{5}^{}B$

(c) for the nutron bombardment on $_{19}^{40}K$ ejecting an alpha particle.

10. The four isotopes ^{16}O, ^{28}Si, ^{40}Ca and ^{56}Fe make up around 85 % of the atoms in the earth's crust. ^{2}H, ^{6}Li, ^{10}B, ^{14}N and ^{50}V contribute less than 1 % of all the atoms in the earth's crust. Comment.

11. Write a concise account of the different techniques by which isotopes can be separated.

12. Write short notes on the following:
(a) isotope diulution analysis
(b) activation analysis
(c) Szilard-Chalmers reaction
(d) nuclear cross-section

13. Can electrolysis be the basis of separation of isotopes of any element? If so, give details of one such separation.

14. Give a comparative account of the nuclear binding energy curve and packing fraction curve. What informations are available from these curves?

15. A sample of radioactive sodium (half-life $= 14.8$ hr) is injected into the body of an animal. How many hours will be required for the activity to come to one-tenth of its original intensity, assuming that none is excreted? (Ans. $\simeq 49$ hr)

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Addenda

Page 16: *after second line*

Einstein proposed in 1905 that the photoelectric emission (also called photo-electric effect) could be adequately explained if light was made up of discrete particles or photons of energy $h\nu$. He argued that a photon of frequency ν and energy $h\nu$ hits a metal surface and transfers its energy to an electron. A certain quantity, say ϵ of this energy is utilised to overcome the attractive force between the electron and the positive nuclei of the metal. The remaining part of the trans-ferred energy goes alongwith the ejected electron in the form of kinetic energy. Then we can write:

$$h\nu = \epsilon + \tfrac{1}{2}mv^2$$

It is easily understood that in order that the photon can eject an electron it must possess a minimum energy ϵ. In terms of frequency we can write $\epsilon = h\nu_0$ so that the total energy $h\nu$ must be the sum of $h\nu_0$ and $\tfrac{1}{2}mv^2$.

$$h\nu = h\nu_0 + \tfrac{1}{2}mv^2$$
$$\therefore \quad \tfrac{1}{2}mv^2 = h\nu - h\nu_0$$

It has been observed that if the kinetic energy of the ejected electron ($\tfrac{1}{2}mv^2$) is plotted against frequency ν of the striking photon a straight line is obtained whose slope is equal to h, the Planck's constant and the intercept gives $h\nu_0$.

An addiitonal observation was that the number of the photoelectrons increases with the intensity of the light. This means that the intensity of light has to be associated with the number of photons arriving at a point per unit of time (cf: page 27).

Page 30: *at the end of the first paragraph*

(5) An s-electron has a greater probability of being very close to the nucleus than a p electron. Again a p electron is likely to be nearer to the nucleus than a d electron.

An inquisitive reader may ask at this stage that while the plot of the radial probability density function $4\pi r^2 \psi^2$ versus radius passes through one or more

maxima depending on the type of the orbital what happens when ψ or ψ^2 is plotted against r. In order to have an answer to this we have to take the expression of the wave function of an orbital. For simplicity we have the 1s wave function (cf: Appendix, Part II).
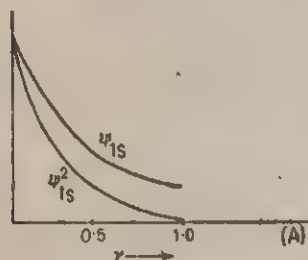
Fig. 1. Plots of ψ_{1s} and ψ_1^2 versus r for hydrogen atom.

$$\psi_{1s} = \left(\frac{1}{\pi}\right)^{\frac{1}{2}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

For the hydrogen atom Z is equal to 1 so that we have:

$$\psi_{1s} = \left(\frac{1}{\pi}\right)^{\frac{1}{2}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

so that the square of the wave function becomes:

$$\psi_{1s}^2 = \frac{1}{\pi} \left(\frac{1}{a_0}\right)^{3} e^{-2r/a_0}$$

It is seen that the above expressions are independent of angular coordinates θ and ϕ. Both ψ_{1s} and ψ_{1s}^2 go to maxima as r goes to zero although the magnitude of ψ_{1s} is larger than ψ_{1s}^2. When r goes to zero the exponential terms become 1 so that
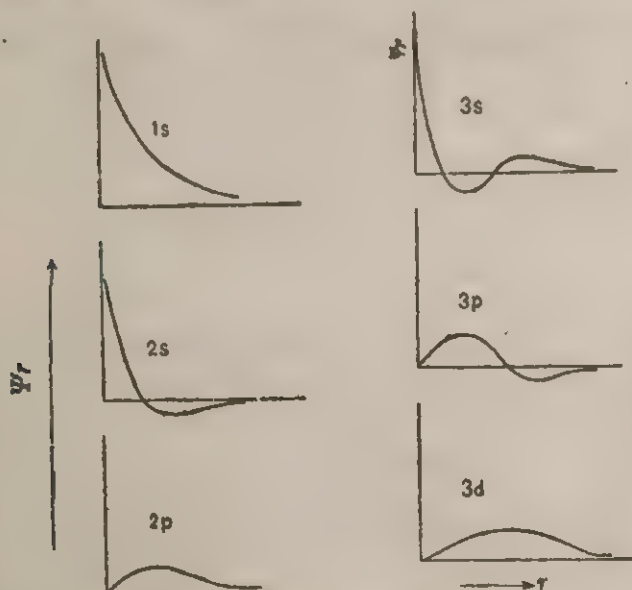
Fig. 2. Plots of radial wave functions for 1s, 2s, 2p, 3s, 3p and 3d orbitals

ψ_{1s} and ψ_{1s}^2 depend on π and a_0 raised to appropriate powers. Both the ψ_{1s} and ψ_{1s}^2 decrease as r increases (Fig 1). However the ψ_{1s}^2 plot indicates that the volume element close to the nucleus has the highest probability of having the electron.

One can easily appreciate that the ψ vs r plot or ψ^2 vs r plots of other orbitals will have different shapes as the wave functions are different (Fig 2). It is of interest

to note that the s orbitals alone have maximum values for ψ at the nucleus *i.e.* when r is zero. But the 2p, 3p and the 3d orbitals have their ψ as zero at the nucleus. This gives us a clue that the s orbitals penetrate the nucleus most while the p and d orbitals cannot penetrate the nucleus. This means that the s orbital electrons can efficiently screen the nuclear charge from other electrons compared to the p and d electrons.

Page 79: *at the end of section* 4.4

Slater's rules: Slater had proposed some empirical set of rules to calculate the screening constant σ of various electrons present in different orbitals of an atom or an ion. Once we get at the value of σ it is easy enough to find out the effective nuclear charge Z*.

The rules given below are valid for an electron in the (ns, np) level.

1. The first thing to do is to write out the electronic configuration of the atom or the ion in the following order and groupings:

(1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p) etc.

It may be noted that so far as the screening effect (also called the shielding effect) is concerned the s and p electrons belonging to the same principal quantum shell have the same effect as advocated by Slater.

2. An electron in a certain (ns, np) level is screened only by electrons in the same level and by electrons of lower energy levels. Electrons lying above (ns, np), level do not screen any (ns, np) electron to any extent. Higher energy electrons have no screening effect on any lower energy electrons.

3. Electrons of an (ns, np) level shield a valence electron in the same group by 0.35 each. This is also true for electrons of the nd or nf *i.e.* for electrons in the same group.

4. Electrons belonging to one lower quantum shell *i.e.* (n−1) shell shield the valence electron by 0.85 each.

5. Electrons belonging to (n−2) or still lower quantum shell shield the valence electron by 1.0 each. This means the screening effect is complete.

The above rules apply quite well while estimating the screening effect of s and p orbitals. However when a d or an f electron is being shielded the second and the third rules remain as they are but the fourth and the fifth rules are substituted by a new sixth one.

6. All electrons below the nd or nf level contribute 1.0 each towards the screening constant.

For the sake of getting familiar with actual application of the Slater's rules we work out the following Z* and σ.

I. Find out the effective nuclear charge of the sodium atom.

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We have to evaluate the screening effect experienced by the valence electron of the sodium atom. Obviously the valence electron will be excluded from the calculation.

$$\text{Na atom: } (1s)^2 (2s, 2p)^8 (3s)^1$$
$$\sigma = (2 \times 1.00) \quad + (8 \times 0.85) = 8.8$$
$$Z^* = 11 \ (i.e. \ Z) \quad - 8.8 = 2.2$$

II. Evaluate the Z^* of sodium ion.

$$\text{Na}^+ \text{ion: } (1s)^2 (2s, 2p)^8$$
$$\sigma = (2 \times 0.85) \quad + (8 \times 0.35) = 4.5$$
$$Z^* = 11-4.5 = 6.5$$

III. Evaluate the Z^* of magnesium ion.

$$\text{Mg}^{2+} \text{ion: } (1s)^2 (2s, 2p)^8$$
$$\sigma = (2 \times 0.85) \quad + (8 \times 0.35) = 4.5$$
$$Z^* = 12-4.5 = 7.5$$

IV. Find out the σ and Z^* of potassium ion.

$$\text{K}^+ \text{ion} = (1s)^2 (2s, 2p)^8 (3s, 3p)^8$$
$$\sigma = (2 \times 1.0) + (8 \times 0.85) + (8 \times 0.35) = 11.6$$
$$Z^* = 19-11.6 = 7.5$$

V. Estimate the σ and Z^* of the valence electron of the fluorine atom.

$$\text{F atom; } (1s)^2 (2s, 2p)^7$$

The valence electron has to be left out of our estimation.

$$\sigma = (2 \times 0.85) + (6 \times 0.35) = 3.8$$
$$Z^* = 9-3.8 = 5.2$$

VI. Calculate the Z^* of the fluoride ion.

$$\text{F}^- \text{ion: } (1s)^2 (2s, 2p)^8$$
$$\sigma = (2 \times 0.85) + (8 \times 0.35) = 4.5$$
$$Z^* = 9-4.5 = 4.5$$

VII. Calculate the effective nuclear charge of the hydrogen atom.

Hydrogen atom has a single $1s$ valence electron. There is no other electron to screen (i.e. shield, it from the nuclear charge of the single proton.

$$\sigma = 0$$
$$Z^* = 1.0-0 = 1.0$$

Thus the hydrogen electron sees the full nuclear charge of the nucleus i.e. the electron is totally exposed to the proton.

VIII. Estimate the screening constant for the outermost 4s electron of vanadium.

Vanadium has an atomic number 23 and the electron distribuion according to Slater's rule is:

$$(1s)^2 (2s, 2p)^8 (3s, 3p)^8 (3d)^3 (4s^2)$$

We have to consider only one of the two 4s electrons.

$$\sigma = (2 \times 1.0) + (8 \times 1.0) + (8 \times 0.85) + (3 \times 0.85) + (1 \times 0.35)$$
$$= 19.7$$
$$Z^* = 23 - 19.7 = 3.3$$

IX. Evaluate the effective nuclear charge of vanadium (II).

Vanadium (II): $(1s)^2 (2s, 2p)^8 (3s, 3p)^8 (3d)^3$

$$\sigma = (2 \times 1.0) + (8 \times 1.0) + (8 \times 1.0) + (3 \times 0.35) = 19.05$$
$$Z^* = 23 - 19.05 = 3.95$$

X. Calculate the screening constant and effective nuclear charge experienced by a d electron of copper (II) ion.

Copper (II): $(1s)^2 (2s, 2p)^8 (3s, 3p)^8 (3d)^9$

$$\sigma = (2 \times 1.00) + (8 \times 1.0) + (8 \times 1.00) + (8 \times 0.35) = 20.80$$
$$Z^* = 29 - 20.80 = 8.20$$

Page 88 : *footnote to Table* 5.1

Interchange kJ/mole and K cal/mole

Page 93: *at the end of section* 5.2.2

Valence Bond Theory of the Hydrogen Molecule: A Simple Treatment based on Wave Functions:

While discussing the covalent bonding of the hydrogen molecule we have mentioned that at the optimum distance of 0.74A there is overlap of the 1s orbitals of the two individual hydrogen atoms. Under such overlap condition there is a great probability of finding the two electrons in between the nuclei. However, though poor, there is certainly some probability of finding both the electrons on the orbital of one and the same hydrogen atom. In that case one of the earlier hydrogen atoms will behave as though it were a hydride ion and the other hydrogen atom will then obviously be a positive hydrogen cation. Valence bond description of the H_2 molecule takes into consideration all these situations.

Let the two hydrogen atoms be H_A and H_B and the electron belonging to the two atoms be numbered (1) and (2) respectively. The corresponding wave functions be ψ_A and ψ_B respectively. Let us assume that initially the two hydrogen atoms are at infinite distance so that there can be no interaction between the two wave functions ψ_A and ψ_B. Under such condition we can represent the total system by the relation:

$$\psi = \psi_A \psi_B$$

It is necessary to appreciate that each wave function has a corresponding energy which can be evaluated with the aid of the Schrodinger equation (cf; Appendix I, Part II):

$$H\psi = E\psi$$

where H is the Hamiltonian operator which takes the second partial derivative of the wave function ψ, adds them together, multiplies by $-h^2/8\pi^2m$ and then adds the product of ψ and the potential energy V of the electron – proton system.

$$H\psi = \left[\frac{-h^2}{8\pi^2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V\right]\psi = E\psi$$

Since we have placed our two hydrogen atoms at large distance the total energy of the system must be the sum of the two individual hydrogen atom energies. This can be demonstrated assuming that H represents the Hamiltonian of the total system. Then we can write the following relations:

$$H\psi = E\psi$$
$$H(\psi_A\psi_B) = \psi_A H\psi_B + \psi_B H\psi_A$$

It follows from Schrodinger relation that $H\psi_A$ and $H\psi_B$ will equate to $E_A\psi_A$ and $E_B\psi_B$. So we have:

$$H(\psi_A\,\psi_B) = E_B\psi_A\psi_B + E_A\psi_B\psi_A$$
$$= (E_A + E_B)(\psi_A\psi_B) = 2E_H\psi$$

Thus for the two non-interacting H atoms the total energy: $E = 2E_H$

So far, however, no bonding interaction has taken place. The product wave function will still stay good when we bring the two atoms closer together. Then there will arise the possibility of the two electrons to exchange places. This situation will admit of the following two wave functions:

$$\psi_I = \psi_A(1)\,\psi_B(2) \text{ and } \psi_{II} = \psi_A(2)\,\psi_B(1)$$

where (1) and (2) represent the two hydrogen electrons as described at the beginning, since ψ_I and ψ_{II} are equally likely because of indistinguishability of electrons then a combination of the two, called $\psi_{covalent}$, will be equally likely:

$$\psi_{covalent} = \psi_I + \psi_{II} = \psi_A(1)\,\psi_B(2) + \psi_A(2)\,\psi_B(1)$$

Such wave equation can be solved for energy with the help of Schrodinger relation $H\psi = E\psi$ as a function of separating distance r between the two hydrogen atoms. The evaluated energy is observed to be lower than the sum of the two non-interacting hydrogen atom energies. $\psi_{covalent}$ will mostly represent the H_2 molecule i.e. the shared pair covalent bond. However there will be a small probability that both the electrons will be found on the orbital of an individual hydrogen atom. This can be represented as:

$$\psi_{ionic} = \psi_A(1)\,\psi_A(2) + \psi_B(1)\,\psi_B(2)$$
$$[= H_A^-\,H_B^+ + H_B^-\,H_A^+]$$

It may, however, be noted that since both the hydrogen atoms have the same electronegativity the contribution of ψ_{Ionic} towards the final energy will be small. But $\psi_{covalent}$ actually recognises that the two electrons (1) and (2) are being shared between the orbitals of the two atoms. In order for Pauli exclusion principle to be valid lowering of energy will occur i.e. a stable combination will occur only when the two electrons share the orbitals with their spins opposed to each other.

At the end of Page 96

Equivalent hybrid orbitals and non-equivalent hybrid orbitals: Hybrid orbitals may be classified under two heads: (a) equivalent hybrid orbitals and (b) non-equivalent hybrid orbitals. Equivalent hybrid orbitals are those where the percentage contribution of the combining atomic orbitals remains the same in all the hybrid orbitals. In other words the composition in respect of contribution of the different types of orbitals is identical. Thus in the two linear hybrid orbitals of sp type contribution of s and p atomic orbitals is the same (50 %). In sp^2 hybrid orbitals all the three planar hybrid orbitals have 33 % s character and 66 % p character. Similarly all the four hybrid orbitals of the sp^3 type have 25 % s character and 75 % p character. All equivalent hybrid orbitals are identical in their orientation in space with respect to each other. Thus the two sp hybrid orbitals are relatively at 180°, the three sp^2 hybrid orbitals are at 120° to each other and the four sp^3 hybrid orbitals are at 109° to each other. The octahedral d^2sp^3 or sp^3d^2 hybrid orbitals are also equivalent. The bond lengths and bond strengths are usually the same for the equivalent hybrid orbitals.

In the case of trigonal bipyramid we have the hybridisation dsp^3. This hybridisation gives three strong equatorial bonds (s, px, py) and two relatively weaker axial bonds (p_z, d_z^2). Bond lengths and bond strengths are different in the equatorial and axial plane. Square pyramidal hybridisation, d^2sp^2, is also made of four strong square planar (dsp^2) and the d_z^2 orbital. Once again bond lengths and strengths are different in equatorial and axial planes. Thus dsp^3 (trigonal bipyramid) and d^2sp^2 (square pyramid) are examples of non-equivalent hybrid orbitals.

Page 107: *At the end of fourth paragraph*

Although melting points predict ionic structures for SnF_4 and AlF_3 recent structural studies indicate that these compounds are polymeric (octahedral) covalent. Thus SnF_4 has a structure with four bridging equatorial fluorines and

two non-bridging axial fluorines coordinated to tin. In AlF_3 each aluminium is linked to as many as six fluorines, all the fluorines being bridging in nature.
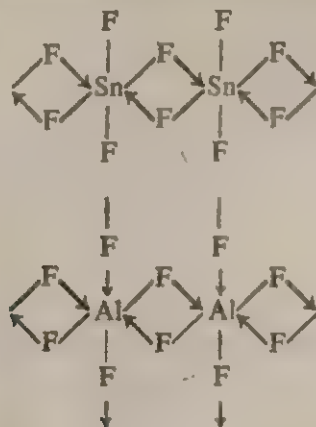
At the end of Page 131

Bent's rule: Bent has formulated a rule about the weightage of *s* character and *p* character in hybrid orbitals of a central atom, which is dictated by electropositive and electronegative substituents attached to the central atom. As originally proposed this runs as:
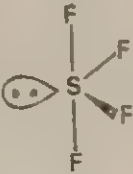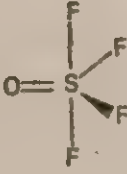
Atomic s character tends to concentrate in orbitals that are directed towards electropositive groups and atomic p character tends to concentrate in orbitals that are directed towards electronegative groups.

Bent's rule appears to be capable of explaining some refinements in bond angles over that predicted by VSEPR model. But before we present an example or two the reader is advised to recall that percent *s* character and percent *p* character have a say in determining the bond angle. The greater *s* character is the greater is the bond angle while the greater the *p* character of hybrid orbital the smaller is the bond angle.

Hybridisation	% s Character	% p Character	Bond angle
sp	50	50	180
sp^2	33	66	120
sp^3	25	75	109

The structure and the bond angles of SF_4 and OSF_4 are given below. In SF_4 molecule there is a lone pair and a lone pair, as we have seen, prefers an equatorial position. The axial FSF angle is 173° which is just 7° compressed from the ideal 180°. This can be explained on VSEPR model being caused by heavier repulsion by the lone pair in the equatorial plane. But the equatorial FSF angle is 101° which is compressed by as much as 19° from the idealised 120°. VSEPR tells us

that 90° interaction between the equatorial lone pair and the axial fluorine must be greater than 120° interaction between the equatorial lone pair and the equatorial fluorines. It is here that Bent's rule makes an improvement over VSEPR. The

Axial FSF bond angle (idealised = 180°)	173°	164°
Equatorial FSF bond angle (idealised = 120°)	101°	115°

lone pair is under the sole control of a single nucleus and this may be viewed as a substituent with an effective electronegativity of zero. Therefore it is most likely that the lone pair attracts more s character than the equatorial bond pairs. Thus for the equatorial bond pair the p character is more than that predicted by sp^2 hybridisation. Hence with increasing p character the equatorial FSF bond angle should decrease.

In OSF_4 the axial FSF bond angle is 164° i.e. 16° less than the idealised 180°. This decrease according to VSEPR may be attributed to repulsion by the $O = S$ double bond. However the equatorial FSF bond angle 115° is quite close to the idealised 120°. Here Bent's rule is again useful. Instead of a lone pair in SF_4 we have $- O$ in OSF_4. Oxygen being very electronegative p character will predominate i.e. the equatorial bonds will be much more close to sp^2 than in SF_4. Hence the sp^2 bonds in OSF_4 are very nearly comparable and bond angles are close to 120° (actually 115°).

Another example where Bent's rule comes to our aid is the molecule $OClF_3$. The equatorial OClF bond angle is 109° which is significantly shorter than the expected 120° based on sp^2 hyprid orbitals. This sharp difference is not easily explained by VSEPR on the basis of the repulsive effect of the lone pair. A double bond is quite fat and is expected to be quite close to a lone pair in repulsive effect. However Bent's rule predicts that since the lone pair is a 'substituent' with practically zero electronegativity so it will have more s character. This means that the equatorial oxygen and fluorine will have more p character and hence the equatorial bond angle OClF is substantially

equatorial OCl F bond angle = 109° (idealised 120°)

lower than 120°. However this lowering is not as severe as 101° for the equatorial FSF in SF_4. This is easily explained when we consider the electronegativity

difference between sulphur and fluorines (~ 1.5) as against the difference between chlorine and the oxygen (~ 0.5) and fluorine (~ 1.0).

Page 211: Structures (10 — III) and (10 — IV) should be corrected as shown below:

(10–III)   (10–IV)
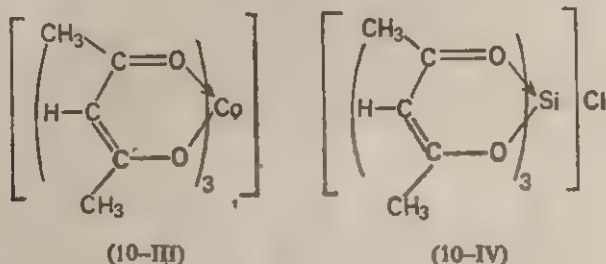
Page 239: *at the end of the fourth paragraph*

It can be guessed that if H_2O of $[Ti(H_2O)_6]^{3+}$ is substituted by a stronger ligand, say by dipyridyl giving $[Ti(dipy)_3]^{3+}$, then light of much higher energy (presumably of the violet region; $\sim \lambda = 400$ nm; $\sim 25,000$ cm^{-1}; ~ 25 κk) will be required to effect the $t_{2g} \rightarrow e_{\rho}$ electronic transition since Δ will now be much higher. The transmitted light will be correspondingly of lower energy and thus the observed colour will be yellow-green or so. Thus we have a simple crystal field explanation of changing colour of a complex with change in the coordinating ligand, assuming however the geometry remains the same. This is, in fact, how the spectrochemical series is obtained.

It is also of interest to note that high spin cobalt (III) ($3d^6$) fluoro complex $K_3 [CoF_6]$ looks blue while all low spin octahedral complexes of cobalt (III) (eg: $[Co(NH_3)_6] Cl_3$) are yellow to orange. Evidently $K_3 [CoF_6]$ absorbs low energy light and transmits high energy light while the diamagnetic complex does the reverse i.e. absorbs high energy light and transmits low energy light. A simple undergraduate level explanation is that for the high spin complex Δ is less than the pairing energy P of cobalt (III) while for the low spin complex Δ is much larger than P i.e. Δ (l.s.) $\gg \Delta$(h.s.). Hence different amounts of energy are required for the electronic transitions in the two spin states, thereby showing varying colours. However this explanation is too simple. For an exact explanation one has to make use of the Tanabe–Sugano diagrams of h. s. d^6 (Fig. 11.10) and l.s. d^6 (Fig. 11.11.).

Page 279: *Last line:* Read "L vector and μ_l vector" for "S vector and μ_l vector".

Page 295: *Twenty third line:* Read "momenta become zero" for "moment become a zero".

Page 300: *seventh line:* Read "$^{231}_{90}$Th and $^{234}_{90}$Th" for "$^{231}_{93}$Th and $^{234}_{92}$Th".

Page 227: *at the end of the last paragraph*

The value of Dq in an octahedral geometry has been calculated with the following results:

$$D = \frac{35ez}{4a^5} \text{ and } q = \frac{2e\overline{r^4}}{105}$$

Where

e = electronic charge

z = magnitude of the charge on the ligand

a = metal—ligand distance

$\overline{r^4}$ = mean fourth power radius of the d electrons of the central ion

However this theoretical value of Dq has little value as the terms are difficult to determine. In reality the value of Dq is evaluated from electronic spectral measurements and Tanabe-Sugano diagrams (page, 276).

Page 233 ; *at the end of the sixth line*

The *CFSE* (= 12 Dq) of [Ni (H$_2$O)$_6$]$^{2+}$ is $-10,200$ cm^{-1} while that (= 8Dq_t) of [Ni cl$_4$]^2 is -3254 cm^{-1} so that the difference is about $-7,000$ cm^{-1} in favour of the octahedral aquo complex. The corresponding values of [Co (H$_2$O)$_6$]$^{2+}$ (= 8Dq) and of [Cocl$_4$]$^{2-}$ (= 12 Dq_t) are -7440 cm^{-1} and -3774 cm^{-1} so that the difference is about -3700 cm^{-1} in favour of the aquo complex. Thus nickel (II) favours octahedral geometry to tetrahedral geometry much more than does cobalt (II).

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